THE STRUCTURES OF AROMATIC POLYCYCLIC COMPOUNDS.

by

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GENERAL INDEX

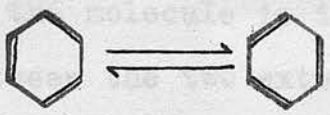
INTRODUCTION

The Arrangement of Double Bonds in Aromatic Compounds.

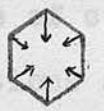
The problem of the constitution of aromatic compounds was first attacked many years ago by Kekulé, who, in his classic paper on the constitution of benzene, began a controversy which has not even yet been finally settled. With the development of chemical knowledge, many methods, both physical and chemical, have been applied to the elucidation of the structures of benzene, and of the more complex polycyclic aromatic compounds. From the physical side, studies of X-Ray spectra, and measurements of dipole moments and refractivities, have considerably increased the literature on the subject.

Since the more complex structures of naphthalene, acenaphthene and other hydrocarbons may be considered as "fused" benzene rings, it is interesting to note the

development of the theory of the structure of the simple benzene units. Several formulae for benzene call for serious consideration, the most important of these being:-



KEKULE.



ARMSTRONG-
BAMBERGER.

CLAUS.

Baeyer

LADENBURG.

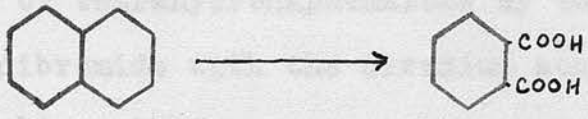
DEWAR.

In proposing his formula for benzene, Kekulé was guided by two regularities which had already been established in connection with the chemistry of aromatic substances. The first of these was the fact that mono-substitution products of benzene existed in one form only, from which it followed that all six hydrogen atoms were chemically equivalent. Secondly, disubstitution products occurred in three isomeric forms, a fact which could most readily be accounted for by considering the benzene molecule as a closed chain of six carbon atoms, to each of which was attached an atom of hydrogen. The position of the fourth valency gave rise to some doubt, and Kekulé suggested that each carbon atom was linked to one of its two neighbours by a double bond. In a mole-

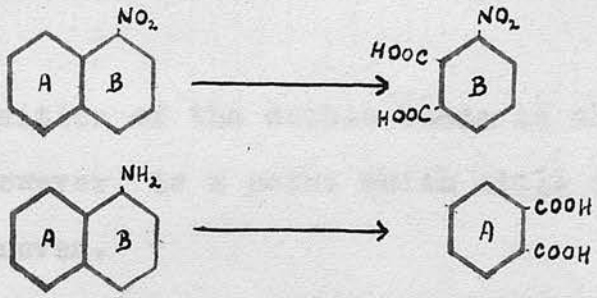
cule of this structure the di-derivatives 1:2 and 1:6 would necessarily differ, on account of the arrangement of the double bonds, and to overcome this difficulty Kekulé advanced his oscillation hypothesis. According to this, the molecule is in a state of continual oscillation between the two extreme positions shown above.

The most striking feature of benzene is its remarkable stability towards specific olefinic reagents, and but for this fact, the Kekulé formula, as modified by the oscillation hypothesis, would long ago have found general acceptance. Attempts have been made to explain these anomalies, and as a result, Armstrong and Bamberger, and Claus have proposed formulae in which the fourth valencies of the carbon atoms, which cannot be utilised for ring formation or for combination with other atoms, are directed towards the centre of the ring, where they neutralize one another. The exact meaning of these centric valencies, however, is not stated, and although they may account for the stability of benzene, when applied to more complex polynuclear ring systems, they do not harmonise with the chemical properties of these compounds. Despite all attempts to disprove it, the formula of Kekulé is still retained as that giving the best possible representation of the chemical properties of benzene. (Pauling and Wheland, J. Chem. Physics, 1933, 1, 362.)

Proof that the molecule of naphthalene has two benzene rings with two adjacent carbon atoms in common, is furnished both by degradation of the molecule by oxidation, and by its synthesis from benzene derivatives. When naphthalene itself is oxidised it yields phthalic acid:-

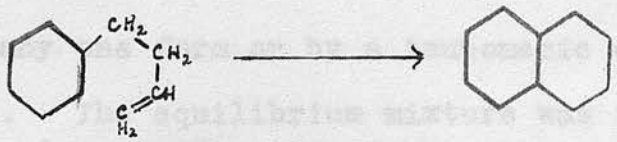


Similarly, α-nitronaphthalene yields nitrophthalic acid on oxidation, but if the nitro-compound is first reduced to the amino-compound, then phthalic acid and not aminophthalic acid is the oxidation product.



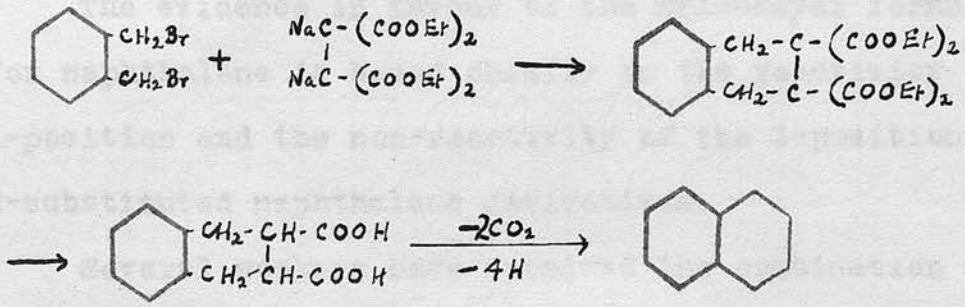
Therefore in one case ring A was oxidised away and in the other case ring B was oxidised to give the carboxyl groups of phthalic acid.

Confirmation of the fact that naphthalene contains two benzene nuclei is given by the synthesis of naphthalene by passing the vapour of phenyl-butylene over red-hot lime:-



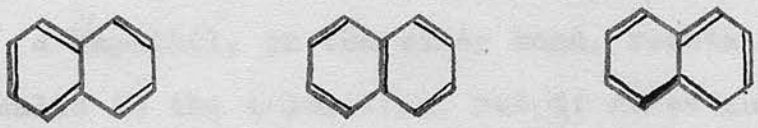
Phenyl butylene Naphthalene

Again, Baeyer and Perkin obtained naphthalene and derivatives of tetrahydronaphthalene by the reaction of o-xylylene dibromide with the disodium compound of ethane tetracarboxylic ester:-



The position of the double bonds in the naphthalene molecule, however, is a point which still cannot be regarded as proven.

If the Kekulé benzene formula be applied to naphthalene there are three possible arrangements of bonds:-



I II III

When considered in the light of the oscillation modification, however, we see that naphthalene may be repres-

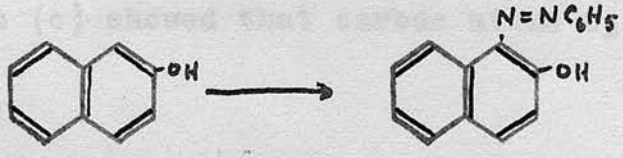
ented by any one form or by a tautomeric equilibrium of all three. The equilibrium mixture was first suggested by Erdmann (Ann., 1893, 275, 191). In formulae I and III it will be seen that only one of the rings is really a benzene ring, whereas in formula II, proposed by Erlenmeyer in 1866, both rings are truly aromatic.

Evidence for Erlenmeyer Formula.

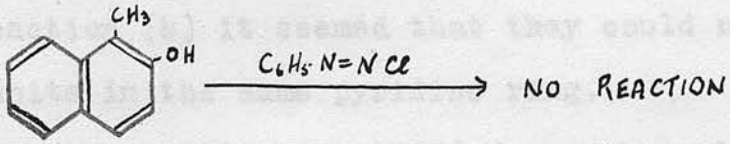
The evidence in favour of the Erlenmeyer formula for naphthalene is based chiefly on the reactivity of the 1-position and the non-reactivity of the 3-position in 2-substituted naphthalene derivatives.

Several workers have examined the combination of various substituted and unsubstituted naphthols with diazonium salts. β-naphthol itself reacts with these salts in the α-position, and it was found that if first substituted in the α-position with a group which could not easily be split off, it did not couple at all. If a labile substituent such as chlorine was attached to the α-position then it was displaced by the diazonium group. α-naphthol, on the other hand, reacts with diazonium salts in the 4-position, but if first substituted in this position, the union took place through C_2.

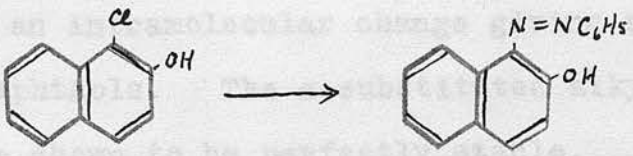
(a)



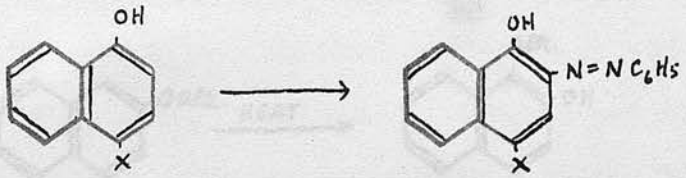
(b) Fries and Hubner (Ber., 1906, 39, 442)



(c) Hewitt and Mitchell (J.C.S., 1912, 89, 1172)



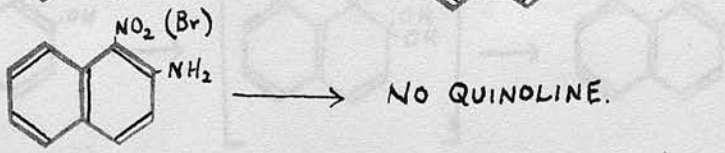
(d)



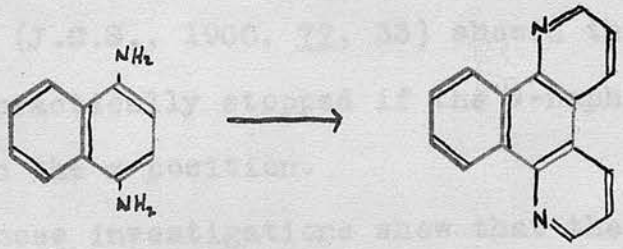
Marckwald (Ann., 1894, 279, 1) studied the Skraup reaction on β-naphthylamine, α-bromo-β-naphthylamine, α-nitro-β-naphthylamine, and α_1-α_2-diaminonaphthalene. He found that a group in the α-position in β-naphthylamine prevented quinoline formation.

(a)

(b)



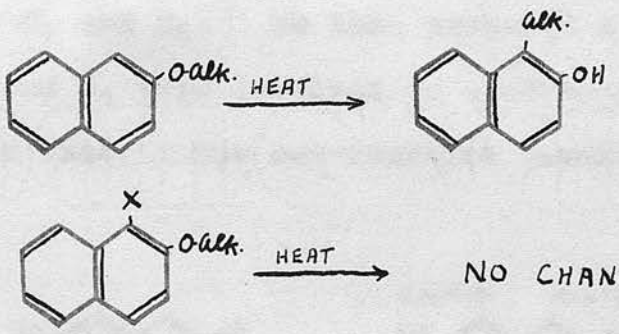
(c)



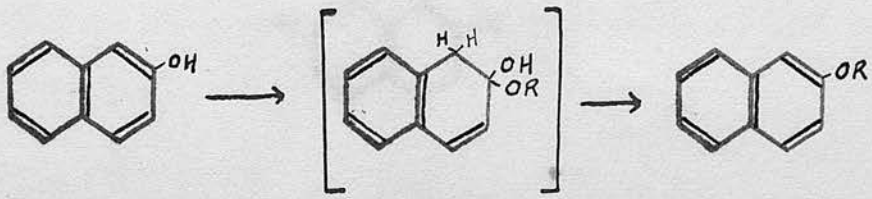
Reaction (c) showed that carbon atoms C_2 and C_3

could take part in quinoline formation simultaneously, but from reaction (b) it seemed that they could not both form units in the same pyridine ring.

Claisen (Ber., 1912, 45, 3157) found that when the alkyl ethers of β-naphthol were subjected to heat, they underwent an intramolecular change giving rise to α-alkyl β-naphthols. The α-substituted alkyl ethers, however, were shown to be perfectly stable.



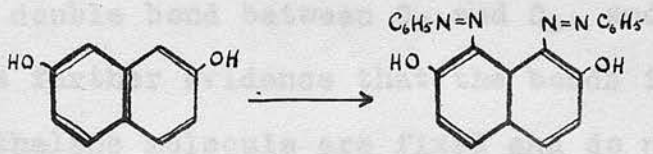
The following mechanism for the etherification of β-naphthol with an alcohol and mineral acid, has been suggested by Henry (Ber., 1877, 10, 2041), and Wegscheider (Monatschefte, 1895, 16, 140).

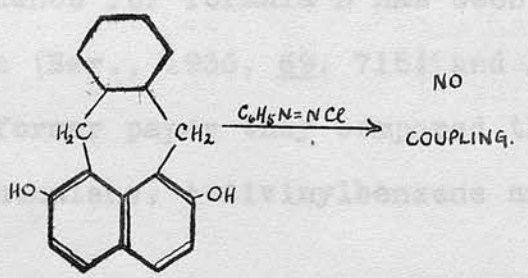


Davis (J.C.S., 1900, 77, 33) showed that etherification was practically stopped if the β-naphthol was substituted in the α-position.

All these investigations show that the two positions ortho to the β-carbon atom in naphthalene derivatives

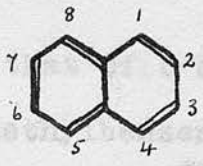
are not equivalent. They demonstrate the probable existence of a double bond between C_1 and C_2, and of a single bond between C_2 and C_3. If the naphthalene molecule is symmetrical, then this is almost conclusive evidence in favour of the Erlenmeyer formula, so Fieser, (J.A.C.S., 1935, 57, 1459) set out to prove the symmetry of the molecule. He first showed that in 2:7-dihydroxynaphthalene, diazonium salts attached themselves to carbon atoms C_1 and C_8. He then prepared a compound in which C_1 and C_8 were involved in a seven-membered ring, and showed that it was non-reactive towards diazonium salts.



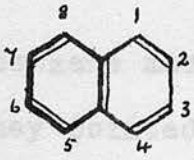


Moreover, the alkyl ethers of this compound were stable towards heat.

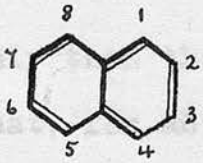
The previous work had shown the presence of a double bond between C_1 and C_2, but this was not incompatible with form A, or with a tautomeric equilibrium mixture of A and B, A and C, B and C, or A, B and C.



A

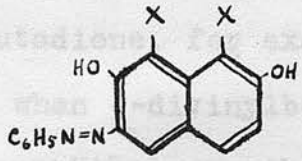


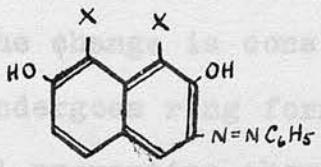
B



C

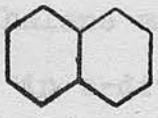
If Fieser's compound, however, existed either wholly or partly in the form A or C, then we would expect the diazo residue to couple as shown below.



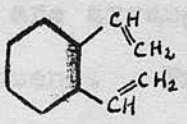


Thus B, the Erlenmeyer formula seems to be the only one which is compatible with all the evidence. Also the lack of a double bond between C_2 and C_3, and between C_6 and C_7, is further evidence that the bonds in a substituted naphthalene molecule are fixed and do not oscillate.

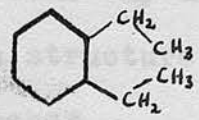
Still more evidence for formula B has been supplied by Fries and Bestian (Ber., 1936, 69, 715; and Ann., 1937, 533, 72). In the former paper they compared the absorption spectra of naphthalene, o-divinylbenzene and o-diethylbenzene.



Naphthalene



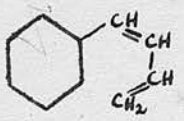
o-divinylbenzene



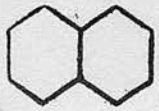
o-diethylbenzene

Their measurements of molar diffraction and dispersion showed that the structure of naphthalene res-

embled that of o-divinylbenzene more closely than that of o-diethylbenzene. They pointed out that, for an aromatic compound with an unsaturated sidechain, the optical properties which they studied generally changed considerably when ring closure was affected, indicating rearrangement of the double bonds in the complete molecule. In the case of the formation of naphthalene from phenylbutadiene, for example, the change is considerable, whereas when o-divinylbenzene undergoes ring formation to give naphthalene, the optical properties show practically no change.

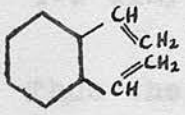


Phenylbutadiene

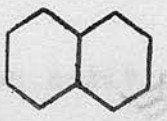


Naphthalene

Different optical properties



o-divinylbenzene



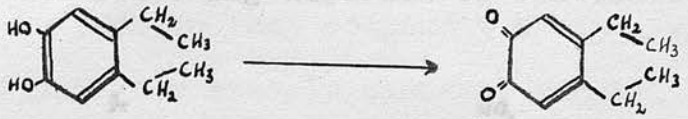
Naphthalene

Similar optical properties

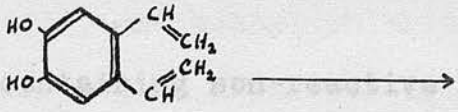
Thus they conclude that the double bonds in the naphthalene molecule are arranged in the same way as those in o-divinylbenzene. Proof of the structure of o-divinylbenzene is given in the second paper.

Oxidation of a dihydroxy aromatic compound to the corresponding quinone is known to depend in some way on the presence of a double bond between the carbon atoms

to which the hydroxyl groups are attached. Fries and Bestian prepared 4:5-dihydroxy-1:2-diethylbenzene and 4:5-dihydroxy-1:2-divinylbenzene, and oxidised them under the same conditions with silver oxide. Only the former compound yielded a quinone, so it was concluded that in this case a double bond existed between C_4 and C_5, whereas in the divinyl derivative C_4 and C_5 must be linked by a single bond.



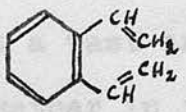
4:5-dihydroxy-1:2-diethylbenzene



No quinone

4:5-dihydroxy-1:2-divinylbenzene

Thus the formula for o-divinylbenzene must be,

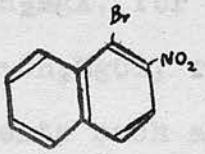


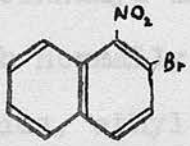
and that for naphthalene,

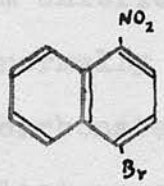
The Erlenmeyer structure is also supported by the work of McLeish and Campbell (J.C.S., 1937, 1103) on the

reactivities of the halogen in various nitro-bromo derivatives of naphthalene. They found that the halogen was reactive, if, according to the Erlenmeyer formula, the carbon atom to which it was attached was linked to the carbon atom bearing the nitro group by a double bond or conjugated system of double bonds. If, however, this linkage was by means of a single bond, the halogen was found to be non-reactive (cf. p. 24).

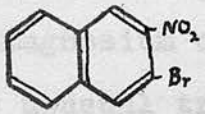
Thus the following derivatives contained reactive halogen:-

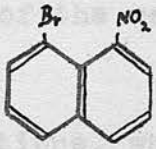


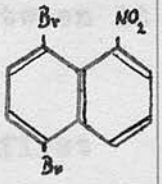




while those containing non-reactive halogen were:-







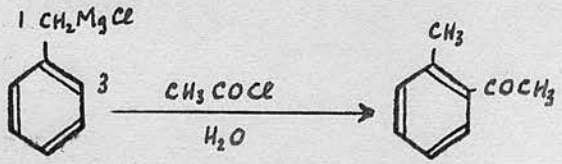
Thus we see that a vast amount of chemical evidence has been gathered together in favour of the Erlenmeyer formula for naphthalene.

Recently a study has been made by Gilman and co-workers (J.A.C.S., 1927, 49, 1825; 1929, 51, 3475; 1931, 53, 3541; 1932, 54, 345, 647), of reactions involving rearrangements of some organo-magnesium halides.

Although not undertaken with a view to establishing the positions of double bonds in molecules, their results give further confirmation of the presence of a double bond between C_1 and C_2 in naphthalene.

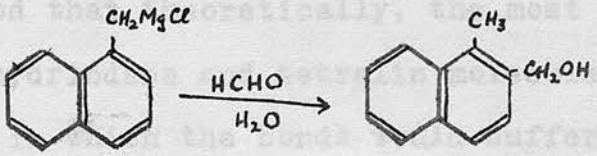
They have shown that compounds of the type $>\overset{3}{C}=\overset{2}{C}\overset{1}{-}CH_2MgX$, for example cinnamyl magnesium chloride $C_6H_5CH=CH\cdot CH_2MgCl$, react both normally and abnormally with reagents such as aldehydes, ethyl chlorocarbonate, acetic anhydride, and acetyl chloride. The last named has been shown to give a particularly high percentage of abnormal product in the case of the reaction between it and benzylmagnesium chloride.

These unusual transformations, which were first examined in aromatic compounds containing an unsaturated sidechain, have been found to occur also in purely aromatic compounds by the above workers, who have examined the reactions of benzylmagnesium chloride and of α-naphthyl-methylmagnesium chloride. In the case of the aromatic methylmagnesium halides, the rearrangement involves the nuclear introduction of a substituent and may be simply illustrated by the following reaction:-



With such systems as the above, there is a modified allylic type, in the sense that the -MgCl grouping is attached to a carbon atom which is in turn connected to an olefinic or olefinic-like group. In accordance with such a three-carbon system, a correlation is understandable with an aliphatic allylic rearrangement where a group on carbon atom I suffers rearrangement or replacement to give a product with the group on carbon atom III.

Similarly it was found that the reaction between α-naphthylmethylmagnesium halide and formaldehyde, yielded α-methyl β-naphthyl carbinol.

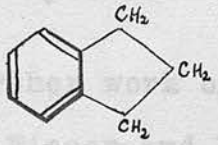


Obviously if the presence of an olefinic-like group in the β-position to the reactive -MgX grouping, is necessary for the transformation to take place, then in the naphthalene molecule a double bond must exist between the α and β carbon atoms.

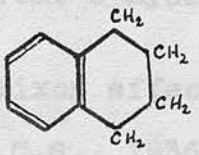
Fixation of Bonds.

Further evidence that in some compounds at least, the bonds seem to be in definite fixed positions, has been obtained chiefly from the examination of semi-reduced compounds such as tetralin and hydrindene.

Mills and Nixon (J.C.S., 1930, 2510) have examined the problem from a purely theoretical point of view and quote experimental evidence in favour of their deductions. They calculated the sizes of the angles between two single bonds and between a single bond and a double bond, and showed that theoretically, the most stable states of the hydrindene and tetralin molecules, that is, the states in which the bonds would suffer least strain, are represented by the following arrangements of single and double bonds:-



Hydrindene



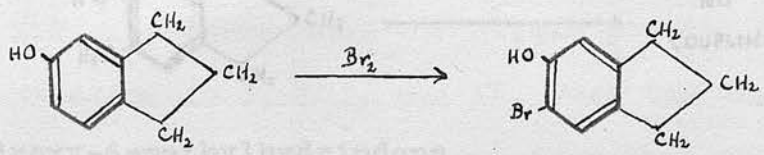
tetralin

The experimental evidence quoted in favour of these assumptions is as follows.

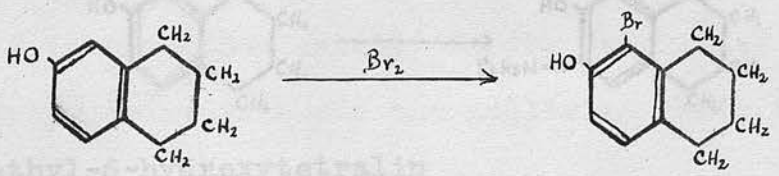
It is well known that diazotised amines and also bromine react with enolic compounds in such a way that the substituting group is introduced at the carbon atom which is linked to that bearing the hydroxyl group by a double bond. The coupling of diazonium compounds with

phenols, (already quoted above in the case of the naphthols) and the bromination of phenols, is closely analogous to this.

Mills and Nixon inferred that, if their theoretical conclusions were correct, diazotised amines and bromine should substitute in the 6-position in 5-hydroxyhydrindene, and in the 5-position in 6-hydroxytetralin. This, in fact, was found to be the case:-



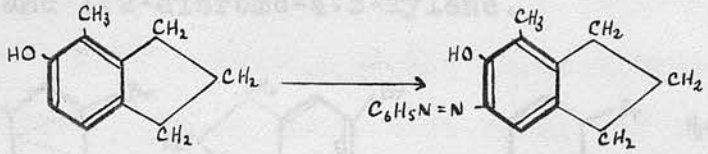
5-hydroxyhydrindene 6-bromo-5-hydroxyhydrindene



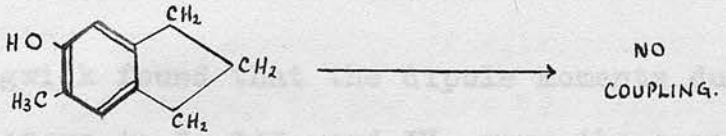
6-hydroxytetralin 5-bromo-6-hydroxytetralin

Further work on the Mills-Nixon effect has been done by Fieser and Lothrop (J.A.C.S., 1936, 58, 2050). They tested the coupling reaction with diazotised amines, of β-hydroxy derivatives of hydrindene and of tetralin with one ortho position blocked with a methyl group, and the other ortho position free, with a view to determining if both ortho positions were capable of constituting enolic groups, or if there was any fixation of the bonds as a result of the spatial requirements of the attached alicyclic rings. (Mills-Nixon effect)

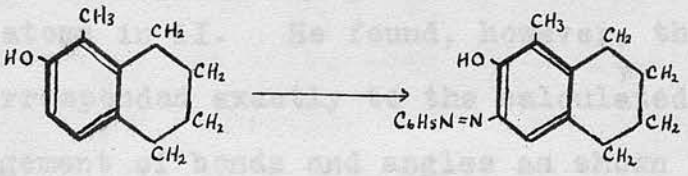
Their results, which are shown below, indicated that hydrindene had a rigid bond structure, but that tetralin, like benzene, can react in both Kekulé forms.



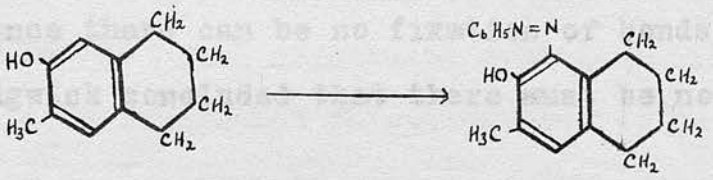
4-methyl-5-hydroxyhydrindene



5-hydroxy-6-methylhydrindene

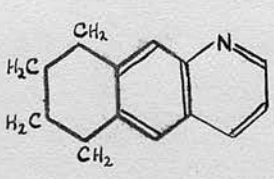


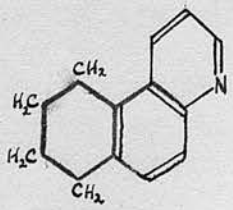
5-methyl-6-hydroxytetralin



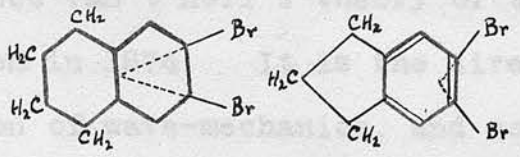
6-hydroxy-7-methyltetralin

Still more evidence that the bonds in tetralin are not fixed has been provided by von Braun and Grubner (Ber., 1922, 55, 1710). They subjected ar-β-amino tetralin to a Skraup reaction and found that two quinolines were formed. These were identified by means of their picrates and found to be:-





Sidgwick (J.C.S., 1936, 1534) has recently compared the dipole moments of 5:6-dibromohydrindene and 6:7-dibromotetralin, with the dipole moments of o-dibromobenzene and 1:2-dibromo-4:5-xylene.



I II III IV

Sidgwick found that the dipole moments due to the bromine atoms in I, III, and IV, were the same, but that these were quite different from that due to the bromine atoms in II. He found, however, that the value in II corresponded exactly to the calculated value for an arrangement of bonds and angles as shown in the figure.

Since there can be no fixation of bonds in III and IV, Sidgwick concluded that there must be no fixation in I.

We see therefore, that evidence does exist to show that in some compounds, of which hydrindene is an example, the bonds are definitely fixed, while in others there is no such fixation.

Resonance

The conception of resonance is probably the most important development in structural organic chemistry since van't Hoff's theory of the three-dimensional carbon atom in 1874. It is the direct result of the application of wave-mechanics, and could not have been deduced from classical dynamics. According to Sidgwick, (Sidgwick's Organic Chemistry of Nitrogen, by Taylor and Baker) the meaning of the term "resonance" can be simply explained as follows.

If a molecule can have two or more structures in the organic sense of the term, then under certain conditions, its actual state is neither one nor the other, but something intermediate between the two, which partakes to some extent of the properties of both, but cannot be expressed in the usual structural symbols. The molecule is then said to exhibit resonance, and to be a resonance-hybrid of the various structures. The conditions for resonance to be possible between two structures are these:-

I The relative positions of the atoms in space must be nearly the same in both:

II the two must not differ too greatly in stability, that is, both formulae must be reasonably probable:

III the number of paired electrons, (that is, valencies in which two atoms unite by sharing two electrons, one

being contributed by each atom,) must be the same in both forms.

The results of resonance are:-

(a) the molecule has to some extent the properties of each constituent structure, those of the more stable form predominating:

(b) the hybrid has a lower energy content than either of the two structures:

(c) the distances between the atoms are smaller than normal.

Of these, (b) is most important for it implies that resonance must always occur whenever possible, and that its occurrence must always increase the stability of the molecule.

Resonance must not be confused with tautomerism from which it is distinguished in that:-

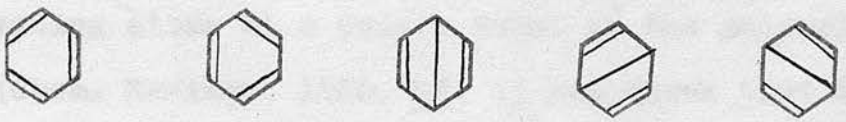
(a) the hybrid is one substance and not a mixture of two:

(b) it can only occur when the atoms in each possible structure occupy nearly the same positions in space:

(c) the hybrid must always be more stable than either of the "mother-forms".

The theory of resonance has been applied to benzene, naphthalene, and other condensed ring systems such as acenaphthene, anthracene, and phenanthrene. (Pauling and Wheland, J. Chem. Physics, 1933, 1, 362; Pauling and Sherman, ibid., 606.)

When applied to benzene, the theory of resonance, as outlined above, shows the possibility of existence of five simple structures with no intersecting bonds. Pauling has named these canonical structures. (J. Chem. Phys., 1933, 1, 280.) They are:-



A B C D E

Of these, A and B are Kekule structures, while C, D, and E are Dewar forms.

It has been shown by solution of the wave-mechanics equations, that for the benzene molecule, the energy of the system is in its ground state if the molecule be considered as a superposition pattern of all five canonical structures, each Kekule form contributing 39% and each Dewar form 7·3%.

With naphthalene, which has forty-two canonical structures, the calculations are much more involved, but the principle is the same as that outlined for benzene.

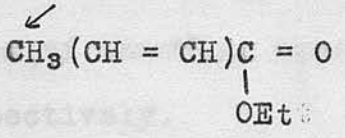
On the resonance theory, therefore, we can give no structural picture of these molecules, although this is not quite in accordance with the observed chemical facts quoted earlier in the Introduction.

This point will be taken up later in the discussion.

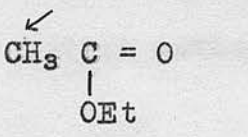
Theory of Activation by Unsaturated Groups

It has long been recognised that, in a molecule containing a system of conjugated double bonds, the influence exerted by any functional group may sometimes be propagated along the chain and make itself apparent by activating atoms at a remote point in the molecule. Fuson, (Chem. Reviews, 1935, 16, 1) has shown that this effect has wide application, and has called the phenomenon "vinylogy".

An illustration of this principle is the fact that the methyl group in ethyl crotonate behaves in some respects as it does when attached directly to the ester group as in ethyl acetate.



Ethyl crotonate

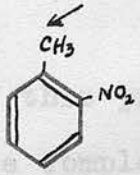


Ethyl acetate

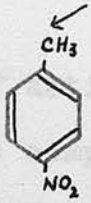
Nitro, nitrile, carboxyl, and all similar unsaturated groups are known to exert an activating effect on the reactivity of other groups in the molecule. Thus the methyl group in nitromethane enters into a wide variety of reactions involving removal of one or more of its hydrogen atoms.

Fusion quotes further application of the principle to the case of the nitrotoluenes. It has been shown by the work of Angeli and others, that the methyl groups

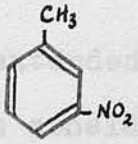
in ortho and para nitrotoluenes are reactive and undergo reactions similar to that of nitromethane. The benzene ring, according to the Kekulé formula, consists of a system of conjugated double bonds, and the above observations are accordingly in agreement with Fuson's principle. Furthermore, as would again be expected, the methyl group in meta-nitrotoluene is non-reactive.



Reactive

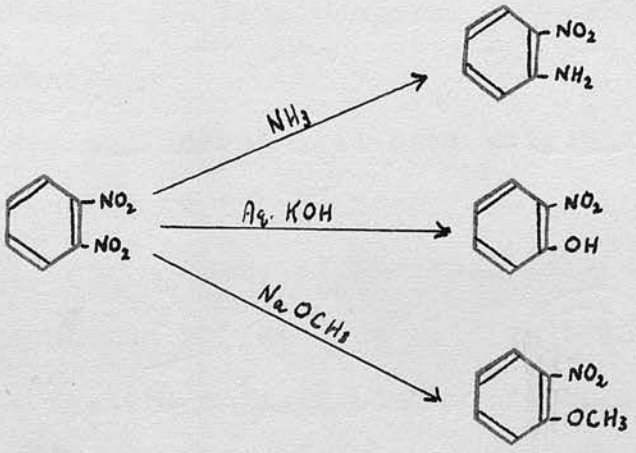


Reactive



Non-reactive.

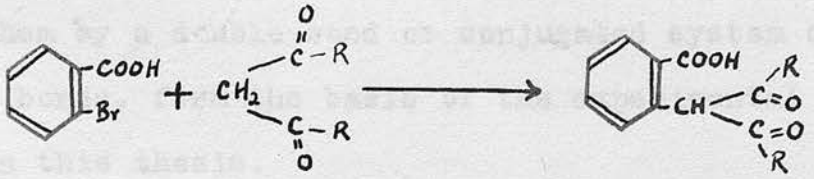
In the case of o-dinitrobenzene, one nitro group can be replaced by amino, hydroxyl, or methoxyl, by means of ammonia, aqueous alkali or sodium methoxide respectively.



In aromatic halogen substituted compounds such as bromobenzene, the halogen atom is highly non-reactive,

but if the molecule is further substituted in the ortho or para positions by an unsaturated group, then the halogen atom becomes reactive.

Thus o-bromobenzoic acid reacts with active methylene compounds as follows:-



If this principle of activation be extended to the more complex aromatic compounds, then considerable evidence should be obtained with regard to the positions of the double bonds in these molecules, and as to whether the bonds are mobile or fixed. This is shown by the work of McLeish and Campbell referred to on p. 12.

Subject of Research.

The reactivities of the carbon atoms situated at the extremities of a double bond, and the activation conferred on halogen atoms by nitro groups separated from them by a double bond or conjugated system of double bonds, form the basis of the experimental evidence in this thesis.

The work may be divided into three sections:

I. Examination of various bromonitro derivatives of acenaphthene, diphenyl, and fluorene, with a view to determining the arrangements of the double bonds in these compounds.

II. Determination of the effect of the presence of other groups on the activation of halogen by nitro groups. For this purpose the activities of halogen in various bromonitrobenzenes were compared with those in bromonitrotoluenes.

III. It was considered that some evidence might be obtained with regard to the structure of the naphthalene molecule, from a study of the reactions of β-naphthylmethyl magnesium halide (See p.14). If this compound underwent transformations similar to that occurring with the α-compound, then α-substituted β-methylnaphthalenes should be obtained. On the other hand if the α-position in the molecule were blocked by a substituent, then,

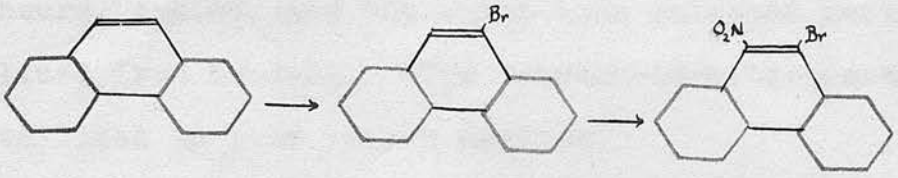
since it is probable that a single bond exists between carbon atoms 2 and 3 in the naphthalene molecule, we would expect to obtain a normal product in this case.

EXPERIMENTAL SECTION

The experimental work carried out is described in the following pages. Yields of products are quoted as percentages of the maximum theoretical amounts obtainable. Melting points are corrected, the thermometer used having been calibrated against short-stemmed "standard thermometers". All new compounds have been analysed by Dr Weiler (Oxford), or in the Department of Medical Chemistry in the University of Edinburgh by Mr. Brown, lecture assistant.

9-Bromo-10-Nitrophenanthrene.

(cf. Austin, J.C.S., 1908, 93, 1760)



(a) Bromination of Phenanthrene:-

Phenanthrene (1 mol) was dissolved in dry chloroform and bromine (2 mols) in the same solvent, was added to the cooled solution. The unstable phenanthrene dibromide quickly crystallised out as a yellow solid. This was filtered off and heated in a beaker on a water-bath till the evolution of copious fumes of HBr ceased. 9-Bromophenanthrene remained as an oil which solidified on cooling. It was recrystallised from light petroleum ether.

Yield theoretical. M.p. 62°C. (Quoted 63°C)

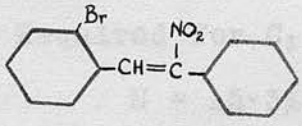
(b) Nitration of 9-bromophenanthrene:-

9-Bromophenanthrene, (5 gms.) was dissolved in hot glacial acetic acid containing a little acetic anhydride, a slight excess of fuming HNO_3 was added and the mixture cooled at once without further heating. The yellow solid which separated, was treated with boiling toluene and filtered from undissolved residue which consisted of 3-nitroanthraquinone. The crude 9-bromo-10-nitrophenanthrene which separated from the filtrate was suspended

in methyl alcohol containing a little stannous chloride in solution. The red liquid was boiled under reflux for two hours, cooled, and the solid thus obtained recrystallised from benzene. The 9-bromo-10-nitrophenanthrene crystallised in pale yellow needles.

Yield very small. M.p. 208°C. (Quoted 209°C)

Attempted preparation of 2-bromo-7'-nitrostilbene.



(a) o-Bromobenzaldehyde.

o-Bromobenzaldehyde was prepared by a method similar to that used by Brady and Lahiri, (J.C.S., 1934, 1956), for the oxidation of 2-nitro-4-tert.-butyltoluene to the corresponding aldehyde.

o-Bromotoluene (5 grams) was added to a mixture of 50 cc. acetic anhydride, 40 cc. glacial acetic acid and 8 cc. concentrated sulphuric acid, and the mixture was cooled to 0°C. Chromium trioxide (20 grams) was added in small portions with shaking, care being taken that the temperature did not exceed 10°C. A few minutes after the last addition of oxidising agent, the mixture was poured on to ice, and the white aldehyde diacetate filtered off. The latter was then hydrolysed by boiling

for one hour with concentrated hydrochloric acid. The acid mixture was diluted, extracted with ether, and on removal of the ether the o-bromobenzaldehyde was distilled.

Yield about 1 gram. (20%)

B.p. 228°C - 230°C. (B.p. quoted 230°C)

o-Bromobenzaldehyde dinitrophenylhydrazone was prepared and found to melt at 199°C - 200°C.

Analysis. Required for $C_{13}H_9N_4O_4Br$

N = 15·3%.

Found N = 15·3%.

(b) Condensation of o-bromobenzaldehyde with phenylnitromethane. (cf. Knoevenagel and Walter, Ber., 1904, 37, 4509)

The above condensation was carried out by heating under reflux for twenty four hours a mixture of o-bromobenzaldehyde (1 gram), phenylnitromethane (0·74 gram), methylamine hydrochloride (0·1 gram), sodium carbonate (0·04 gram), and a few drops of alcohol. On cooling, the reaction mixture was allowed to stand for some time when crystals separated. These were filtered off and recrystallised from ligroin several times.

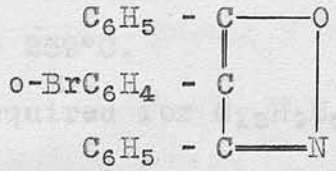
Yield 0·5 gram.

M.p. 135°C.

Analysis.

Found C = 67·4%; H = 4·2%; N = 3·8%; Br = 20·1%.

These figures are not in agreement with those required for the bromonitrostilbene. The compound obtained is probably an isoxazole of the formula



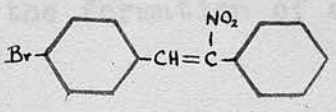
The percentage composition of this compound is in good agreement with the figures obtained above and is as follows.

C = 67·0%; H = 3·7%; N = 3·7%; Br = 21·3%.

Further reference to this compound will be made in the Discussion.

Note. The phenylnitromethane used in the above experiment was prepared by a standard method (Wislicenus and Endres, Ber., 1902, 35, 1757).

Attempted preparation of 4-bromo-7'-nitrostilbene.



(a) p-Bromobenzaldehyde.

p-Bromobenzaldehyde was prepared in exactly the same

manner as the ortho-compound.

The aldehyde crystallised from methyl alcohol in white needles.

Yield 0·5 gram.

M.p. 66°C. (M.p. quoted 67°C)

The compound formed a dinitrophenylhydrazone which melted at 257°C - 259°C.

Analysis Required for $C_{13}H_9N_4O_4Br$, N = 15·3%.

Found N = 15·2%.

(b) Condensation of p-bromobenzaldehyde with phenylnitromethane.

This condensation was carried out as in the previous case.

The yield was 0·5 gram.

M.p. 175°C.

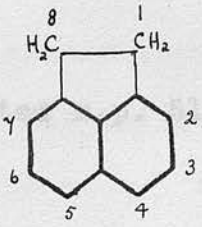
Analysis.

Found C = 73·3%; H = 4·5%; N = 3·9%; Br = 19·6%.

The analysis figures quoted above exclude the possibility of the compound being the required stilbene derivative, and the formation of an isoxazole is again indicated.

ACENAPHTHENE SERIES

Three systems of notation for acenaphthene are given in the literature, probably the most rational being that suggested by Morgan and Stanley (J.S.C.I., 1925, 44, 493T). This system has been employed in the following work and the notation is given below.



Its advantage lies in the fact that it shows the relationship between acenaphthene and the 1:8-disubstituted derivatives of naphthalene.

4-Bromoacenaphthene.

(Cf. Walker, J.C.S., 1912, 101, 958).

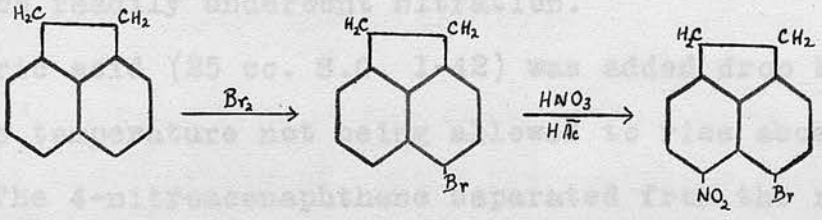
To a solution of 10 grams acenaphthene in 30 cc. ether, was added an ether solution containing the theoretical amount of bromine required for monobromination. The mixture was allowed to stand until the ether evaporated, and the oily solid which remained was then pressed on a porous plate.

The white solid was recrystallised from methyl alcohol.

Yield 50%.

m.p. 50°C. (quoted m.p. 51°C).

4-Bromo-5-nitroacenaphthene.



(Cf. C.A., 1931, 1518).

4-Bromoacenaphthene (8 grams) was dissolved in 40 grams hot glacial acetic acid and the solution was quickly cooled to 10°C. The solution was stirred vigorously and concentrated nitric acid (5 cc.) was slowly run in. The yellow 4-bromo-5-nitroacenaphthene separ-

ated, and was filtered off. Recrystallisation from alcohol gave light yellow needles.

Yield 65%.

m.p. 160°C (m.p. quoted 159°C - 161°C).

Note:- The paper referred to above merely outlines the method of nitration but gives no experimental details.

4-Nitroacenaphthene

(Cf. Morgan, J.S.C.I., 1930, 49, 413T)

A suspension of acenaphthene (50 grams) in glacial acetic acid (400 cc.) was stirred, and heated until a clear solution was obtained. The solution was then cooled rapidly, with stirring, to 10°C. The acenaphthene separated from the solution as a fine crystalline mass which readily underwent nitration.

Nitric acid (25 cc. S.G. 1·42) was added drop by drop, the temperature not being allowed to rise above 10°C. The 4-nitroacenaphthene separated from the reaction mixture as a yellow crystalline mass. This was filtered off, washed well with cold water, and recrystallised from glacial acetic acid, from which it formed fine yellow needles.

Yield 85%.

M.p. 106°C. (m.p. quoted 106°C.)

4-Aminoacenaphthene.

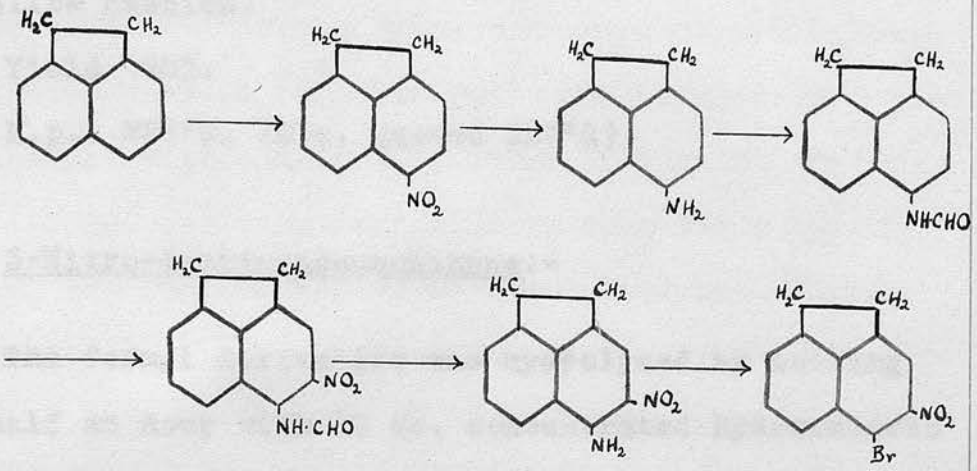
4-Nitroacenaphthene (20 grams) was dissolved in a mixture of alcohol (200 cc.) and water(100 cc.). To the solution, sodium hydrosulphite (100 grams) was added in three portions. After boiling under reflux until the foam was colourless, (about 3 hours) the alcohol was removed by distillation and 100 cc. hot water and 100 cc. concentrated hydrochloric acid were added to the residue. The mixture was boiled, filtered and the residue boiled repeatedly with further amounts of dilute hydrochloric acid. On neutralising the combined filtrates with ammonia, the amine was precipitated. It was filtered, and recrystallised from alcohol or petroleum ether (b.p. 60°C - 80°C) giving colourless needles.

Yield 70%.

M.p. 108°C. (M.p. quoted 108°C.)

Note: In this reduction it was found advisable to use double the quantity of sodium hydrosulphite recommended by Morgan (loc. cit.) and also to boil the solution for a longer time.

3-Nitro-4-bromoacenaphthene.



(a) 4-Formamidoacenaphthene:-

4-Aminoacenaphthene was boiled under reflux for one hour with four times its weight of 90% formic acid. The formyl derivative was precipitated on pouring into water and was recrystallised from dilute alcohol.

Colourless needles.

Yield 92%.

M.p. 172°C. (M.p. quoted 172°C).

(b) 3-Nitro-4-formamidoacenaphthene:-

4-Formamidoacenaphthene (7·5 grams) was dissolved in glacial acetic acid (30 cc.) and the solution was cooled to 10°C. Nitric acid (9 cc. S.G. 1·42) was added gradually with stirring, the temperature not being allowed to exceed 15°C. 3-Nitro-4-formamidoacenaphthene

separated out and was filtered off. On recrystallisation from glacial acetic acid the compound was obtained as yellow needles.

Yield 70%.

M.p. 226°C. (M.p. quoted 227°C).

(c) 3-Nitro-4-aminoacenaphthene:-

The formyl derivative was hydrolysed by boiling for half an hour with 10 cc. concentrated hydrochloric acid in 75 cc. alcohol. The solution became dark red in colour and, on cooling, a quantitative yield of the nitroamine separated out. Recrystallisation from alcohol gave dark red needles.

M.p. 219°C. (M.p. quoted 219°C.).

(d) 3-Nitro-4-bromoacenaphthene:-

The diazotisation and subsequent Sandmeyer reaction were adapted from the work of Hodgson and Walker (J.C.S., 1933, 1621) on 4:4'-dichloro-3:3'-dinitrodiphenyl, and the following procedure found application in many later preparations of a similar type.

Finely powdered sodium nitrite (10% in excess of the calculated quantity), was added slowly to concentrated sulphuric acid (7 cc. per gram) contained in a beaker which was cooled in iced water. When all the

sodium nitrite had been added, the beaker was heated slowly and the contents stirred till the temperature reached 70°C. When solution was complete the mixture was cooled to room temperature. The weighed amount of nitroamine, suspended or dissolved in glacial acetic acid (12 cc. per gram) was stirred into the solution slowly, the temperature being maintained below 30°C. The diazo solution was then run fairly quickly and with stirring into a solution of cuprous bromide in concentrated hydrobromic acid. The mixture was heated on the steam bath till evolution of nitrogen ceased, water was added and the resultant precipitate was extracted with ether and purified.

Diazotisation of 3-nitro-4-aminoacenaphthene:-

4·6 grams 3-nitro-4-aminoacenaphthene.
55 cc. glacial acetic acid.
1·6 grams sodium nitrite.
11 cc. sulphuric acid.

4 grams cuprous bromide.
26 cc. conc. hydrobromic acid.

Crystallisation first from alcohol and then from petroleum ether (b.p. 80°C - 100°C) gave golden yellow

plates.

Yield 66%.

M.p. 143°C. (M.p. quoted by Thompson, Thesis, Edinburgh 1935, 143°C).

2-Nitroacenaphthene.

(Cf. Morgan and Harrison, J.S.C.I., 1930, 49, 415T)

Acenaphthene (200 grams) was dissolved in acetic anhydride (2·5 litres) and the mixture cooled quickly to -5°C. The hydrocarbon was thus obtained in suspension as a very fine precipitate.

A solution of diacetylorthonitric acid was prepared by adding 100 cc. concentrated nitric acid to 1000 cc. acetic anhydride. Considerable heat was evolved and the nitrating mixture was cooled to between 0°C. and -10°C before use.

The suspension of acenaphthene was stirred vigorously by means of a mechanical stirrer, and the diacetylorthonitric acid run in at such a rate that the liquid became clear and free from suspended solid. Throughout the nitration the temperature of the mixture was not allowed to exceed 16°C. On cooling to 10°C the solution deposited crude 2-nitroacenaphthene which was filtered off and recrystallised from alcohol. It cryst-

allised in bright greenish yellow needles.

Yield 21%.

M.p. 151°C (M.p. quoted 151°C).

On pouring the mother-liquor into water a 79% yield of 4-nitroacenaphthene was obtained.

Bromination of 2-nitroacenaphthene.

2-Nitroacenaphthene (5 grams) was dissolved in glacial acetic acid (25 cc.) and the theoretical quantity of bromine required for monobromination was added. The solution was brought to the boiling point and allowed to crystallise. After several recrystallisations from alcohol a compound was obtained in the form of yellow needles.

Yield 2 grams (30%).

M.p. 159°C - 160°C.

Analysis Required for $C_{12}H_8NO_2Br$

N = 5·0% ; Br = 28·7%.

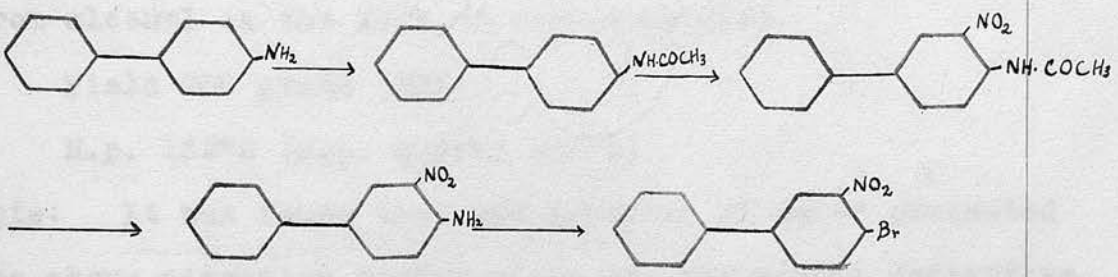
Found N = 5·3% ; Br = 28·7%.

Note: This compound was not orientated due to the small amount available and the difficulty involved. It is probable, however, that it is 2-nitro-5-bromoacenaphthene, as the peri-positions in the molecule are the most

reactive, and the presence of the nitro group would prevent further substitution in that ring. Removal of the nitro group by reduction and diazotisation would fail to distinguish between the 4-bromo and 5-bromo derivatives since both of these would yield 4-bromoacenaphthene. The bromine atom should be unreactive from our point of view both in the 4-bromo and 5-bromo derivatives.

DIPHENYL SERIES.

3-Nitro-4-bromodiphenyl



(a) 4-Acetamidodiphenyl:-

4-Aminodiphenyl (200 grams) was suspended in benzene (200 cc.) and acetic anhydride (121 grams) was added carefully, the mixture being cooled in running water. The acetyl compound separated and after fifteen minutes was filtered at the pump and was well washed with water.

The compound was sufficiently pure for the next stage.

Yield 200 grams (80%).

M.p. 171°C (M.p. quoted 171°C).

(b) 3-Nitro-4-acetamidodiphenyl:-

The dry acetyl compound (180 grams) was dissolved in glacial acetic acid (1800 cc.) and the solution warmed to 70°C on a water bath. Fuming nitric acid (200 grams S.G. 1·51), mixed with an equal volume of glacial acetic acid, was gradually stirred into the solution, which darkened in colour. After keeping at 70°C for one hour the mixture was poured into twice its volume of cold water. The yellow 3-nitro-4-acetamidodiphenyl was precipitated and filtered off. It crystallised from alcohol in the form of yellow needles.

Yield 200 grams (70%).

M.p. 132°C (M.p. quoted 132°C).

Note: It was found that the presence of water prevented the above nitration taking place and the acetyl derivative was therefore thoroughly dried before proceeding with the nitration.

(c) 3-Nitro-4-aminodiphenyl:-

The acetyl derivative was boiled with one litre of alcohol and a solution of 100 grams potassium hydroxide in

125 cc. water was added. The contents of the flask immediately became deep red in colour, and in a few minutes a dark red mass of crystals separated, which was filtered off and washed with 30% alcohol.

Yield 166 grams (Theoretical).

M.p. 168°C - 169°C (M.p. quoted 169°C).

(d) 3-Nitro-4-bromodiphenyl:-

The 3-nitro-4-aminodiphenyl was diazotised and the Sandmeyer reaction carried out according to the method of Hodgson and Walker (loc. cit.).

Data: 6·5 grams 3-nitro-4-aminodiphenyl

78 cc. glacial acetic acid

2·4 grams sodium nitrite

17 cc. conc. sulphuric acid

15 grams cuprous bromide

45 cc. conc. hydrobromic acid.

On recrystallisation from petroleum ether (b.p. 40°C - 60°C) the compound crystallised in long yellow prismatic needles.

Yield 4·5 grams (54%).

M.p. 41°C - 42°C.

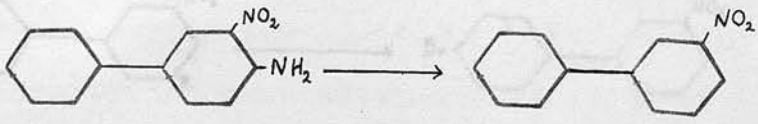
Analysis:-

Required for $C_{12}H_8NO_2Br$

N = 5·0% ; Br = 28·7%.

Found N = 4·9% ; Br = 27·6%.

3-Nitrodiphenyl



3-Nitro-4-aminodiphenyl (160 grams) was added to a mixture of 95% alcohol (390 cc.) and concentrated sulphuric acid (58 cc.). The mixture, after being heated till solution was complete, was cooled in iced water and vigorously stirred. A solution of sodium nitrite (94 cc.) containing 60 grams sodium nitrite in 100 cc. solution, was allowed to flow in drop by drop during a period of twenty minutes, and the reaction mixture was then allowed to stand for three hours in the cold. Copper powder (6 grams) was next added in portions, the flask being kept cool in water. The mixture gradually warmed up to 40°C while nitrogen and acetaldehyde were rapidly evolved. The alcohol was distilled off and the residue distilled in a current of superheated steam, the flask being immersed in an oil bath above 200°C.

The compound crystallised from alcohol in yellow

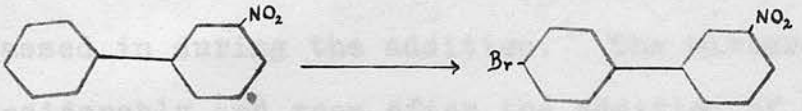
needles.

Yield 60 grams (40%).

M.p. 62°C (M.p. quoted 62°C).

3-Nitro-4'-bromodiphenyl

(Cf. Blakey and Scarborough, J.C.S., 1927, 3008)

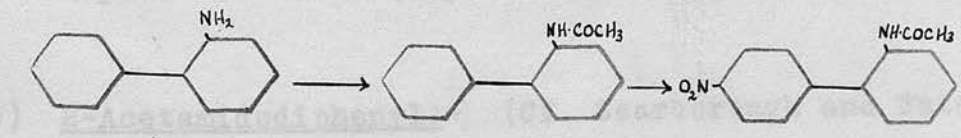


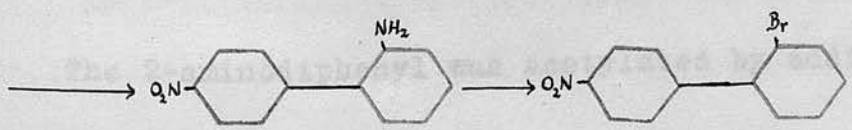
3-Nitrodiphenyl (5 grams) was ground to a fine powder with 0·5 gram ferric chloride and bromine (7 grams) was added. When the mass had cooled, water was added, and the mixture heated on the water bath for half an hour to complete the reaction, and cooled. A solid was obtained which crystallised from alcohol in yellow plates.

Yield theoretical.

M.p. 95°C (M.p. quoted 95°C).

2-Bromo-4'-nitrodiphenyl





(a) 2-Aminodiphenyl:- (Cf. Sako, Bull. Chem. Soc. Japan, Feb. 1934, 64)

2-Nitrodiphenyl (100 grams) was added in small quantities at a time during a period of one hour, to a solution prepared by passing dry hydrochloric acid gas into a mixture of crystalline stannous chloride (440 grams) and alcohol (500 cc.). Hydrochloric acid gas was passed in during the addition. The mixture heated up considerably and soon after the addition of the nitro compound was completed, the double compound of the amine and stannous chloride began to separate in the form of white needles. These were filtered on the following day and contained about 60% of the theoretical amount of the amine. Concentration of the filtrate yielded more of the double salt. The crystals were treated with 40% potassium hydroxide and the 2-aminodiphenyl liberated extracted with ether. Evaporation of the ether gave a white solid which was distilled in vacuo.

Yield 90%.

B.p. 170°C/15 mm.

M.p. 49°C - 50°C (M.p. quoted 50°C).

(b) 2-Acetamidodiphenyl:- (Cf. Scarborough and Waters, J.C.S., 1927, 91).

The 2-aminodiphenyl was acetylated by adding acetyl

chloride (75 grams) drop by drop to a solution of the base (80 grams) in pyridine (400 grams) at 0°C. After twenty minutes the solution was poured into excess ice-cold dilute hydrochloric acid. The precipitated 2-acetamidodiphenyl was filtered off and crystallised from petroleum ether (b.p. 60°C - 80°C) in large prismatic needles.

Yield theoretical.

M.p. 121°C (M.p. quoted 121°C).

(c) 2-Acetamido-4'-nitrodiphenyl:-

15 grams of the above compound were dissolved in a mixture of 15 cc. glacial acetic acid and 30 cc. concentrated sulphuric acid. The solution was cooled to 0°C and fuming nitric acid (6 cc. S.G. 1·51) diluted with glacial acetic acid (14 cc.) was run in slowly. After standing for one hour the solution was poured on to ice. The nitro compound was filtered, washed with dilute sodium carbonate solution and fractionally crystallised from alcohol, giving pale yellow needles.

Yield 11 grams (61%).

M.p. 199°C (M.p. quoted 199°C).

(d) 2-Amino-4'-nitrodiphenyl:-

The 2-acetamido-4'-nitrodiphenyl was hydrolysed by boiling with 10% alcoholic hydrochloric acid for half an

hour. On cooling the nitro-amine crystallised out quantitatively.

Orange-red needles from alcohol.

M.p. 158°C (M.p. quoted 158°C).

(e) 2-Bromo-4'-nitrodiphenyl:-

The method of Hodgson and Walker was used in the diazotisation and was followed by a Sandmeyer reaction.

Data: 5 grams 2-amino-4'-nitrodiphenyl
60 cc. glacial acetic acid
1·8 grams sodium nitrite
12·5 cc. conc. sulphuric acid.

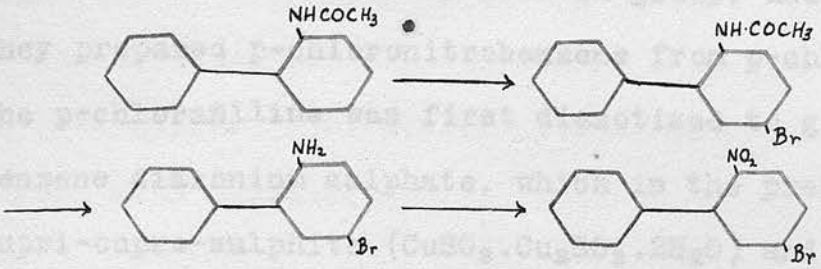
3 grams cuprous bromide
10 cc. conc. hydrobromic acid.

A considerable amount of nitrophenol was formed in the reaction and this was removed by shaking the ether extract with dilute sodium hydroxide. The oily solid remaining on removal of the ether was crystallised from methyl alcohol and then from petroleum ether (b.p. 40°C - 60°C).

Yield 1·5 grams.

M.p. 84°C (M.p. quoted 82·5°C).

2-Nitro-5-bromodiphenyl (loc. cit.)



(a) 2-acetamido-5-bromodiphenyl:-

A cold 10% solution of 2-acetamidodiphenyl (5 grams) in glacial acetic acid was treated with a 10% solution of bromine (3·8 grams) in the same solvent. After twenty four hours the mixture was poured into water and the precipitated 2-acetamido-5-bromodiphenyl, after filtering, was recrystallised from alcohol.

Yield theoretical. White needles.

M.p. 130°C (M.p. quoted 130°C).

(b) 2-Amino5-bromodiphenyl:-

The acetyl compound was hydrolysed by boiling for half-an-hour in 10% alcoholic hydrobromic acid solution. The product crystallised from alcohol in white needles.

Yield theoretical.

M.p. 57°C - 58°C (M.p. quoted 58°C).

(c) 2-Nitro-5-bromodiphenyl:-

Hantzsch and Blagden (Ber., 1900, 33, 2554) described

a method by which they replaced an amino group attached to an aromatic nucleus by a nitro group, and in this way they prepared p-chloronitrobenzene from p-chloraniline. The p-chloraniline was first diazotised to give p-chlorobenzene diazonium sulphate, which in the presence of cupri-cupro-sulphite ($CuSO_3.Cu_2SO_3.2H_2O$) and sodium nitrite reacted to give p-chloronitrobenzene.

A similar reaction was performed on the 2-amino-5-bromodiphenyl.

(1) Preparation of the cupro-cupri-sulphite:-

(Cf. Abegg, Anorganische Chemie, vol. II, Part I, p. 556.)

10 grams copper sulphate crystals were dissolved in 100 cc. water and 2N sodium hydroxide was added until all the copper had been precipitated as hydroxide. Sulphur dioxide gas was passed into the suspension, cooled in iced water, yielding finally a dark green solution. On warming, a red precipitate of cupro-cupri-sulphite was obtained weighing 5 grams.

(2) Preparation of the diazo solution:-

5 grams 2-amino-5-bromodiphenyl

3 cc. conc. sulphuric acid

25 cc. water

2 grams sodium nitrite in solution.

The amine was converted to its sulphate by the addition of the sulphuric acid. A paste of the sulphate in 25 cc. water was transferred to a small flask, cooled in iced water. The sodium nitrite solution was added slowly with stirring.

(3) Introduction of the nitro group:-

10 grams cupro-cupri-sulphite.

32 grams sodium nitrite.

120 cc. water.

This mixture was stirred mechanically in a flask and the diazo solution from (2) was added slowly. A brisk evolution of gas took place and when this had moderated, the flask was heated on the steam bath for half-an-hour to complete the reaction. The solid was then filtered off and extracted with ligroin, from which brown needles crystallised out.

Yield only 0·1 gram.

M.p. 230°C.

Analysis: Required for $C_{12}H_8NO_2Br$

N = 5·0% ; Br = 28·7%.

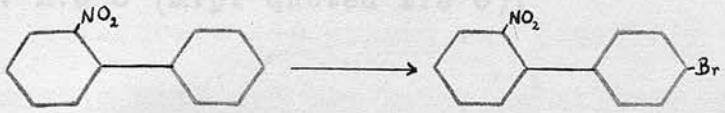
Found N = 5·3% ; Br = 28·9%.

Note: Some doubt was entertained as to the identity of this compound for although the analysis figures agree with the requirements for a nitro-bromodiphenyl, the

melting point of the product was much higher than that of any other compound in the series.

2-Nitro-4'-bromodiphenyl

(Cf. Le Fevre and Turner, J.C.S., 1926, 2041.)



22 grams 2-nitrodiphenyl, 8 grams bromine and 25 cc. water were well mixed and left overnight. The following day the excess bromine was removed with sodium carbonate, the mixture was extracted with ether, and the ether solution dried over calcium chloride. On removal of the ether a viscous brown oil was obtained which, on standing, deposited crystals. The oily solid was transferred to a porous plate and after drying, was crystallised from petroleum ether (b.p. 40°C - 60°C). The 2-nitro-4'-bromodiphenyl was obtained as large yellow prisms.

Yield 10 grams (36%).

M.p. 65°C (M.p. quoted 65°C).

4-Nitro-4'-bromodiphenyl

4-Bromodiphenyl (20 grams) was added to a mixture of nitric acid (45 grams S.G. 1·38) and concentrated

sulphuric acid (20 grams). The mixture was stirred for an hour and a half, the temperature being held between 70°C and 80°C, and was then poured on to ice. The precipitate was filtered, dried by heating and recrystallised from ligroin, giving yellow needles.

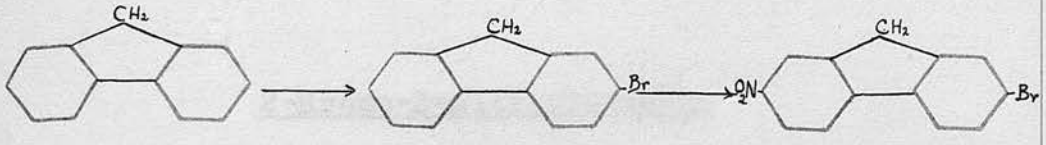
Yield 11 grams (46%).

M.p. 173°C (M.p. quoted 173°C).

FLUORENE SERIES.

2-Bromo-7-nitrofluorene.

(Cf. Courtot and Vignati, Bull. Soc. Chim., 1927, 41, 58)



(a) 2-Bromofluorene:-

Fluorene (15 grams) was dissolved in chloroform, (75 grams) and the solution cooled to between 0°C and 5°C. Bromine (14·5 grams) was introduced drop by drop, the mixture being stirred during the addition. After 24 hours the chloroform was distilled from the blue solution and a crystalline mass obtained. In order to separate any dibromofluorene from the required 2-bromo-

fluorene the white mass was fractionally crystallised from 90% alcohol. The 2-bromofluorene crystallised in white needles.

Yield 11 grams (50%).

M.p. 108°C (M.p. quoted 110°C).

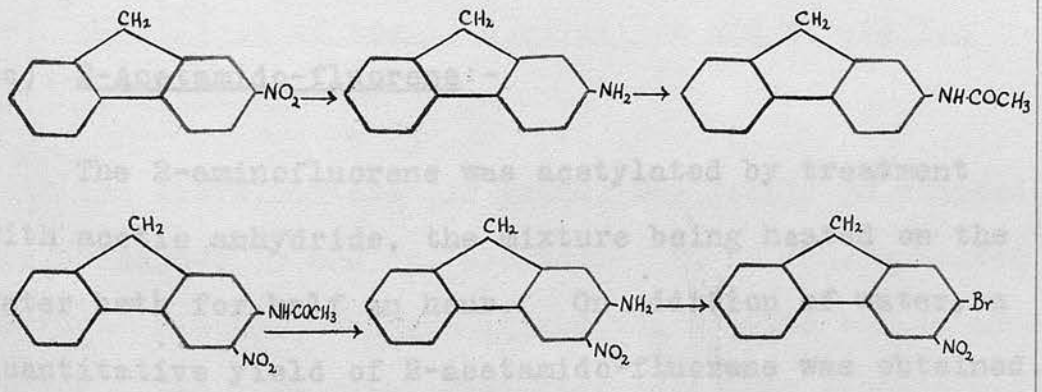
(b) 2-Bromo-7-nitrofluorene:-

2-Bromofluorene (10 grams) was dissolved in 60 cc. glacial acetic acid and the solution stirred whilst nitric acid (10 cc. S.G. 1·42) was run in. The 2-bromo-7-nitrofluorene separated as a yellow crystalline mass. On recrystallisation from benzene the compound was obtained in the form of pale yellow, almost colourless needles.

Yield 6·5 grams (60%).

M.p. 236°C (M.p. quoted 236°C).

2-Bromo-3-nitrofluorene.



(a) 2-Nitrofluorene:-

Fluorene (30 grams) was nitrated in glacial acetic acid solution according to the method detailed in Org.

Synth. 13, 74. During the nitration the temperature was gradually raised to 80°C. If the temperature was allowed to exceed 85°C a highly coloured impure product was obtained. The crude 2-nitrofluorene had a melting point of 154°C - 156°C and was pure enough for reduction to the amine.

Yield 30 grams (80%).

(b) 2-Aminofluorene:- (above reference)

The 2-nitrofluorene prepared above was reduced to 2-aminofluorene with zinc dust (300 grams) and calcium chloride (10 grams in 15 cc. water) in 78% alcohol (1 litre). The 2-aminofluorene crystallised from 50% alcohol in pure white needles.

Yield 20 grams (80%).

M.p. 127°C (M.p. quoted 127·5°C).

(c) 2-Acetamido-fluorene:-

The 2-aminofluorene was acetylated by treatment with acetic anhydride, the mixture being heated on the water bath for half an hour. On addition of water, a quantitative yield of 2-acetamido-fluorene was obtained. Recrystallisation from alcohol gave white needles.

M.p. 190°C. (M.p. quoted 191°C).

(d) Nitration of 2-acetylamidofluorene:-

(Cf. Diels, Schill and Tolson, Ber., 1902, 35, 3285, and Eckert and Langecke, J. prakt. Chem., 1928, 263)

2-Acetamidofluorene (5 grams) was dissolved in 50 cc. hot glacial acetic acid and, with stirring, nitric acid (3·3 grams S.G. 1·42) slowly run into the solution cooled to 52°C. On further cooling the solution deposited a yellow crystalline mass, which was filtered off, washed with 50% acetic acid and with water and dried at 100°C. The crude product, which consisted of a mixture of two isomers, was dissolved in a mixture of boiling acetic acid and alcohol from which it crystallised in yellow needles.

Yield 4 grams.

M.p. (decomp.) 190°C - 200°C.

(e) Hydrolysis of acetyl derivatives and separation of isomers:-

The above mixture (10 grams) was finely pulverised and suspended in 400 cc. alcohol. 20 cc. concentrated hydrochloric acid was run in and the mixture boiled under reflux. At this point some difficulty was experienced in obtaining a clear solution. Much of the yellow solid remained undissolved even after prolonged boiling. The undissolved solid was filtered off and two thirds of the

alcohol distilled from the dark red filtrate, which was then allowed to stand for twelve hours before filtering the red precipitate. This was then warmed on the water bath for two hours with one litre of water and 50 cc. concentrated hydrochloric acid. The 2-amino-3-nitrofluorene remained undissolved while the isomer went into solution as the hydrochloride. The former was filtered off and again treated with dilute hydrochloric acid as above. Finally it was washed with dilute ammonia, then with water, and recrystallised from glacial acetic acid. Deep brown-red needles.

Yield 1·5 grams (18%).

M.p. 204°C - 205°C. (M.p. quoted 206°C).

(f) 2-Bromo-3-nitrofluorene:-

Method:- Hodgson and Walker p.39.

Data: 1·5 grams 2-amino-3-nitrofluorene
18 cc. glacial acetic acid
0·56 gram sodium nitrite
4 cc concentrated sulphuric acid

3·5 grams cuprous bromide
10 cc. conc. hydrobromic acid.

On extraction with ether and removal of the ether, 1·6 grams crude product was obtained (80%). This was

recrystallised from glacial acetic acid and formed dark red needles.

M.p. 120°C - 121°C.

Analysis. Required for $C_{13}H_8NO_2Br$

N = 4·8%; Br = 27·6%.

Found N = 5·0%; Br = 28·4%.

Attempt to prepare 1-Bromo-2-nitrofluorene.

Note:- This attempt resulted in failure to obtain the 1-bromo-2-nitrofluorene but the compounds obtained were further investigated (see Discussion).

(a) 2-p-Toluenesulphonamidofluorene:-

2-Aminofluorene (5 gms.) was dissolved in 15 cc. pyridine, and p-toluenesulphonyl chloride (6 gms.) added. The mixture became hot and assumed a beautiful intense violet colour. The solution was then heated under reflux for one hour and afterwards poured into excess cold dilute hydrochloric acid. The oily mass which separated soon solidified on rubbing with a glass rod. The compound was recrystallised from acetic acid giving colourless plates.

Yield 7 gms. (76%). M.p. 156°C - 157°C.

Analysis. Required for $C_{20}H_{17}NSO_2$

N = 4·2%.

Found N = 4·4%.

(b) Bromination of (a):-

2-p-Toluenesulphonamidofluorene (7 grams - 1 mol) was dissolved in chloroform and bromine (6·7 grams - 2 mols) added. The mixture was heated on the water bath for half an hour and the chloroform then removed by

distillation. The product was recrystallised several times from alcohol.

Yield 8·7 grams (85%). M.p. 198°C - 199°C.

Analysis. Required for $C_{20}H_{15}NBr_2SO_2$

N = 2·8%; Br = 32·4%.

Found N = 2·8%; Br = 31·3%.

(c) Hydrolysis to dibromoaminofluorene:-

The product (b) was dissolved in excess warm concentrated sulphuric acid and the solution poured into a large volume of water. A white flocculent precipitate was obtained and concentrated potassium hydroxide solution was added to the suspension until it was strongly alkaline.

The precipitate was then filtered off and crystallised from alcohol.

Yield almost theoretical. M.p. 145°C.

Analysis. Required for $C_{13}H_9NBr_2$

N = 4·1%; Br = 47·2%.

Found N = 4·1%; Br = 48·7%.

The acetyl derivative of the above compound was prepared and was found to melt at 275°C.

x:x'-Dibromofluorene.

2 grams dibromo-2-aminofluorene

24 cc. glacial acetic acid

·45 gram sodium nitrite

3 cc. conc. sulphuric acid.

The dibromo-2-aminofluorene was diazotised by the method of Hodgson and Walker (p. 39); the diazo solution was then diluted with an equal volume of alcohol, and the temperature of the mixture raised to 80°C. Copious evolution of gas occurred and, when this had ceased the solution was poured into water. The resultant precipitate was filtered off and recrystallised from methyl alcohol.

Yield 0·5 gm. M.p. 129°C.

Analysis. Required for $C_{13}H_8Br_2$

Br = 49·4%.

Found Br = 48·1%.

Note. For reasons outlined in the discussion this compound is probably 3:7-dibromofluorene.

3(?):7(?)-Dibromofluorenone.

The above dibromofluorene (0·2 gram) was boiled under reflux for three hours with sodium dichromate (1 gram) and 2 cc. acetic acid. The mixture, after cooling, was diluted with water and the yellow precipitate filtered off. The compound was recrystallised twice from glacial acetic acid.

Yield 80%.

M.p. 200°C.

Analysis. Required for $C_{13}H_6OBr_2$

Br = 47·3%.

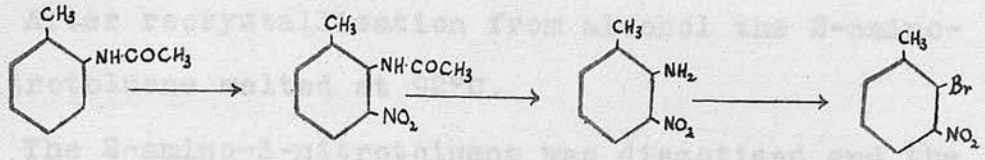
Found Br = 47·45%.

BENZENE SERIES.

The ortho and para bromo-nitrobenzenes were B.D.H. products. The meta derivative was prepared by the standard methods given in the literature.

TOLUENE SERIES.

2-Bromo-3-nitrotoluene.



(a) Nitration and subsequent hydrolysis of aceto-o-toluidide.

(Cf. Cohen and Dakin, J.C.S., 1901, 79, 1127)

15 grams powdered aceto-o-toluidide
50 grams fuming nitric acid
18 grams glacial acetic acid.

The acid mixture was cooled to 15°C and stirred mechanically. The toluidide was added slowly, the temperature being maintained about 15°C. If the mixture is cooled much below this temperature the reaction is suspended and subsequently becomes too vigorous, resulting in the formation of side-products and giving a poor yield of the required substance. When all the toluidide had been added the mixture was allowed to stand for several hours at room temperature, after which it was poured into water. The yellow solid which was precipitated was filtered off and added to 40 cc. concentrated hydrochloric acid in a round-bottomed flask. The mixture was

steam distilled without preliminary heating, a process requiring approximately 6 hours.

Yield 6-7 grams.

After recrystallisation from alcohol the 2-amino-3-nitrotoluene melted at 92°C.

(b) The 2-amino-3-nitrotoluene was diazotised and the subsequent Sandmeyer reaction performed according to the method of Gibson and Johnstone (J.C.S., 1929, 1243).

A suspension of the nitroamine in a mixture of concentrated hydrobromic acid and water was diazotised below 0°C with a solution of sodium nitrite in water. The diazo solution was then rapidly filtered into a solution of cuprous bromide in concentrated hydrobromic acid. The mixture, after heating on the water bath for half-an-hour, was steam distilled and the distillate extracted with ether and worked up.

Data. 2 grams 2-amino-3-nitrotoluene in 1·5 cc. HBr and 4 cc. water

1 gram sodium nitrite in 2 cc. water.

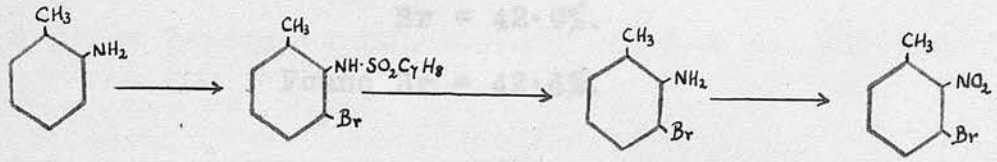
1 gram cuprous bromide

4·5 cc. conc. hydrobromic acid.

Yield 0·6 gram (22%).

M.p. 39°C.

3-Bromo-2-nitrotoluene.



(a) Bromination:-

15 grams o-toluidine

27 grams p-toluene sulphonyl chloride

140 cc. pyridine

7·1 cc. bromine.

The toluidine, toluene sulphonyl chloride and pyridine were mixed in a flask and the bromine added slowly. The mixture was left overnight and poured into dilute hydrochloric acid. The product was crystallised twice from alcohol giving colourless prisms.

M.p. 137°C.

(b) Hydrolysis:-

The 3-bromo-toluidide prepared above was dissolved in hot concentrated sulphuric acid and the solution poured into a large volume of water. The solution was made alkaline and an oily precipitate separated which soon became solid. It was filtered off and crystallised from methyl alcohol in buff-coloured prisms.

Yield 8 grams.

M.p. 57°C - 58°C.

Analysis: Required for C_7H_8BrN

Br = 42·9%.

Found Br = 42·6%.

(c) Diazotisation:- Method as given on p. 51.

8 grams 3-bromo-2-aminotoluene

4·5 cc. concentrated sulphuric acid

40 cc. water

3 grams sodium nitrite.

15 grams cupro-cupri-sulphite

48 grams sodium nitrite

180 cc. water

The product was steam distilled and crystallised from methyl alcohol. Pale yellow prisms.

Yield 3 grams (33%).

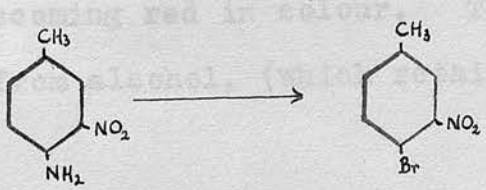
M.p. 54°C.

Analysis: Required for $C_7H_6NO_2Br$

Br = 37·0%.

Found Br = 37·4%.

4-Bromo-3-nitrotoluene.



Method of Gibson and Johnstone p. 66.

5 grams 3-nitro-4-aminotoluene in 3·5 cc. HBr and 9 cc. water.

2·3 grams sodium nitrite in 4 cc. water.

4·5 grams cuprous bromide

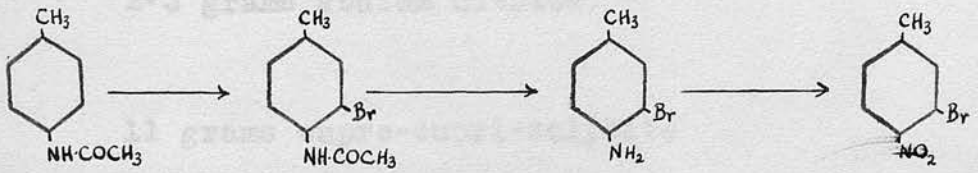
45 cc. conc. hydrobromic acid.

The product crystallised from methyl alcohol in pale yellow needles.

Yield 4·3 grams (60%).

M.p. 32°C - 33°C. (M.p. quoted 34°C).

3-Bromo-4-nitrotoluene.



(a) Bromination of aceto-p-toluidide:-

(Cf. Wroblewsky, Ann., 1873, 168, 153)

Aceto-p-toluidide (20 grams) was covered with water in a round bottomed flask and 7 cc. (21·5 grams) bromine added slowly with shaking. The bromine reacted quickly, the mixture becoming red in colour. The product was crystallised from alcohol, (which retained unchanged

toluidide) and then from boiling water. Colourless needles.

Yield almost theoretical.

M.p. 117°C - 118°C (M.p. quoted 117·5°C).

(b) Hydrolysis to 3-bromo-4-aminotoluene:-

The bromo-aceto-toluidide was mixed with 50 cc. 30% KOH and boiled for about five hours. Bromo-toluidine separated in the flask as an oil.

(c) Diazotisation:- Method as given on p. 51.

6 grams crude 3-bromo-p-toluidine
3·4 cc. conc. sulphuric acid
30 cc. water
2·3 grams sodium nitrite.

11 grams cupro-cupri-sulphite
36 grams sodium nitrite
135 cc. water.

The product, after steam distilling, was crystallised from methyl alcohol.

Very pale yellow needles.

Yield 2 grams (30%).

M.p. 36°C - 37°C.

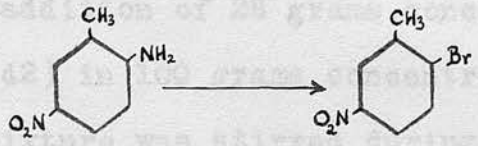
Analysis. Required for $C_7H_6NO_2Br$

Br = 37·0%.

Found Br = 36·7%.

2-Bromo-5-nitrotoluene.

(Method of Gibson and Johnstone p. 66)



5 grams 2-amino-5-nitrotoluene in 3·5 cc. HBr and 9 cc. water.

2·3 grams sodium nitrite in 4 cc. water.

4·5 grams cuprous bromide

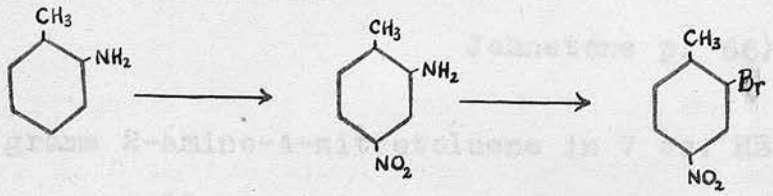
45 cc. conc. hydrobromic acid.

The product, on removal of the ether, was crystallised from alcohol containing a little charcoal, and formed pale yellow prisms.

Yield 6 grams (75%).

M.p. 76°C - 77°C (M.p. quoted 75°C - 76°C)

2-Bromo-4-nitrotoluene.



(a) 2-Amino-4-nitrotoluene:- (Cf. Ullman and Grether, Ber., 1902, 35, 337)

A solution of 30 grams o-toluidine in 450 grams concentrated sulphuric acid was cooled to 0°C and nitrated by the addition of 28 grams concentrated nitric acid (S.G. 1·42) in 100 grams concentrated sulphuric acid. The mixture was stirred during the nitration and subsequently kept for two hours at room temperature. It was then poured on to 600 grams of ice and the mixture stirred. In a short time a thick paste of yellow crystals formed. This was filtered and thoroughly drained at the pump, and then stirred with a slight excess of alkali. 2-Amino-4-nitrotoluene separated in an almost pure state. It was collected, washed with water and crystallised from alcohol.

Yellow prisms.

Yield 34 grams (80%).

M.p. 107°C (M.p. quoted 107°C).

(b) 2-Bromo-4-nitrotoluene:- (Method of Gibson and Johnstone p. 66)

10 grams 2-amino-4-nitrotoluene in 7 cc. HBr + 18 cc. water.

4·6 grams sodium nitrite in 8 cc. water

9 grams cuprous bromide

90 cc. conc. hydrobromic acid.

The product, on crystallisation from alcohol gave very pale yellow, almost colourless prismatic needles.

Yield 10 grams (70%).

M.p. 76°C (M.p. quoted 76°C).

NAPHTHALENE SERIES.

The preparation of β-naphthylcarbinol was first attempted by a method similar to that used by Ziegler (Ber., 1921, 54, 737) in the preparation of α-naphthylcarbinol from α-halogeno-naphthalene.

The naphthalene magnesium halide was treated with gaseous formaldehyde, generated by the dry distillation of paraformaldehyde or trioxymethylene, one and a half times the theoretical quantity being used.

The halogeno naphthalene and trioxymethylene were dried for several days over phosphorus pentoxide before use.

Reaction of β-naphthylmagnesium iodide with formaldehyde.

In a three-necked flask fitted with a stirrer were placed 1 gram magnesium turnings, 10 cc. dry ether, and 0·35 gram ethyl iodide. To the gently boiling mixture was added a solution of 10 grams β-iodonaphthalene in 40 cc. dry ether. (The iodonaphthalene was prepared from β-naphthylamine by the standard methods given in the literature, and melted at 54°C.) A long air condenser was attached to the flask and the third opening was closed by a stopper. When the reaction had moder-

ated, the flask was heated on the water bath for a quarter of an hour to complete the reaction. It was then cooled in a freezing mixture, and the third opening connected to the formaldehyde generating apparatus. The trioxymethylene was boiled and the formaldehyde passed in with stirring.

For some time the reaction seemed to go quite normally, but after a while a white solid and a black tarry substance appeared in the flask. Stirring was continued for some time after all the formaldehyde had been passed in, and then the contents of the flask were treated with water and extracted with ether. On removal of the ether 4½ grams of a brown solid remained, which on recrystallisation (twice) from aqueous methyl alcohol, melted at 185°C. The picrate, m.p. 184°C, showed the compound to be β·β'-dinaphthyl.

M.ps. quoted: β·β'-dinaphthyl 187°C - 188°C;

picrate 184°C.

The experiment was repeated with the preparation of the Grignard in the cold, but the same result was obtained. Repetition using β-bromonaphthalene also failed to give the required alcohol.

In view of the failure to obtain the β-naphthylcarbinol by the above Grignard method, it was decided to attempt its preparation via the aldehyde. Of the two methods tried, only one yielded the aldehyde in

any quantity.

I. β-Naphthaldehyde.

(Cf. Stephen, J.C.S., 1925, 127, 1874)

Anhydrous stannous chloride (19 grams, 1½ mols) was covered with 75 cc. dry ether in a bottle fitted with a ground glass stopper. Dry hydrochloric acid gas was passed in until the mixture separated into two layers, the bottom layer being yellow and viscous.

β-Naphthonitrile (9·8 grams, 1 mol.) was then added and the mixture was shaken for one hour on a mechanical shaker. The semi-solid green mass which separated out was removed from the ether, and decomposed by heating with water for two hours. The mixture was then steam distilled and the distillate extracted with ether. A white solid was obtained melting at 54°C - 57°C. Yield 9·5 grams.

It was thought at first that a quantitative yield of aldehyde had been obtained, since the solid readily formed a dinitrophenylhydrazone, but subsequent investigation showed that the bulk of the product consisted of unchanged nitrile.

Note 1.

The anhydrous stannous chloride was conveniently prepared by dehydrating the ordinary crystalline variety by adding it (1 mol.) slowly to acetic anhydride (2 mols.).

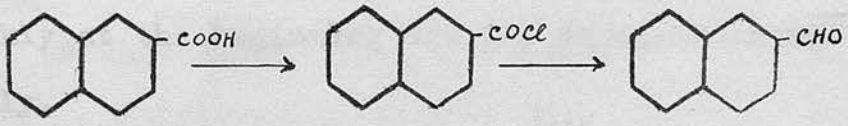
Great heat was evolved in the reaction. The product was filtered, washed free from acetic acid with ether and stored in a desiccator.

Note 2.

Reduction of the supposed aldehyde in alcoholic solution, with zinc dust and hydrochloric acid, or with hydrogen in the presence of palladium-barium sulphate catalyst (apparatus described on p. 79) yielded an interesting specimen of β-methylnaphthalene melting at 40°C (quoted 33°C). This was obtained by sublimation of the reduction product. A picrate was prepared m.p. 118°C (quoted 118°C) and a mixed m.p. with an authentic specimen of β-methylnaphthalene picrate was not depressed. The m.p., however, was depressed on mixing the picrate with picric acid (m.p. of picric acid 122°C).

II.

In this method the β-naphthaldehyde was obtained by the catalytic reduction of β-naphthoyl chloride.



β-Naphthoyl Chloride

(a) 15 grams β-naphthoic acid
30 cc. thionyl chloride

The acid and thionyl chloride were heated under reflux on the water bath for one hour, and the dark coloured liquid poured into a distilling flask. The excess thionyl chloride was distilled off and the acid chloride distilled.

Yield 15 grams. (90%).

b.p. 304° - 306°C. m.p. 42° - 43°C.

(b) 22·8 grams β-naphthoyl chloride

50 cc. xylene

3·5 grams palladium-barium sulphate catalyst.

The acid chloride was dissolved in the xylene in a 100 cc. round-bottomed flask fitted with a ground glass air condenser, and the catalyst added. The solution was kept boiling gently and hydrogen was led through by means of a long glass tube passing down the condenser. Hydrochloric acid gas was evolved and the reaction was stopped when no more could be detected with ammonia. The mixture was then steam distilled, the xylene coming over quickly at the beginning and the β-naphthaldehyde more slowly.

Yield about 10 grams. (51 - 54%).

M.p. 60°C.

The β-naphthaldehyde was identified by means of its phenylhydrazone which melted at 218°C. This compound

crystallised from alcohol in plates which turned a beautiful rose colour on exposure to the air.

The 2:4-dinitrophenylhydrazone of β-naphthaldehyde was also prepared. It formed small orange needles melting at 270°C.

(c) Palladium-Barium Sulphate Catalyst.

(Cf. Houben-Weyl, 1922, 2, 270).

Palladium chloride, (1·7 grams) in 50 cc. water, was added to freshly precipitated barium sulphate (20 grams) in 400 cc. hot water. Formalin (1 gram - 40%) was then added to the mixture, which was made alkaline with dilute sodium hydroxide and heated to the boiling point. When the supernatant liquid was clear and colourless, the grey precipitate was filtered off and washed with hot water until free from alkali. The catalyst was dried in vacuo over potassium hydroxide and stored in a dust-free flask.

Reduction of β-naphthaldehyde to β-naphthylcarbinol.

The method employed was that of catalytic hydrogenation, the apparatus being similar to that described by Buck and Jenkins (J.A.C.S., 1928, 51, 2163).

The reaction bottle (300 cc. capacity) was of thick pyrex glass, capable of withstanding a pressure of 200 lbs. per square inch. It could be connected by means of valves either to an evacuating pump or to a hydrogen gas reservoir. The bottle was securely fixed to a rocking frame which could be shaken at various speeds during the hydrogenation. The apparatus was first of all calibrated for the absorption of one proportion of hydrogen, 0·01 mol. benzoin being used as a standard. Complete hydrogenation to hydrobenzoin corresponded to a fall of 16 lbs./sq. inch on the Bourdon guage connected to the reaction bottle, when the initial pressure was 34 lbs./sq. inch above atmospheric.

The catalytic reduction of aldehydes to alcohols has been worked out in detail by Adams and co-workers (J.A.C.S., 1922, 44, 1397; 1923, 45, 1071; 1924, 46, 1675; 1925, 47, 1047). Their results show that an extremely small concentration of ferric or ferrous chloride in the reaction mixture exercises an amazingly efficient promoter action. The optimum effect was obtained with a concentration of 0·0001 M. ferric or ferrous chloride per 100 cc. reaction mixture. An excess of promoter tends to make the reduction go beyond the alcohol stage.

β-Naphthaldehyde, (6·2 grams, 0·039 mol.) was dissolved in 50 cc. alcohol and 0·5 cc. 0·1 M. aqueous ferric chloride solution added. Adams' platinum catalyst (0·2 gram) was added to the solution; the bottle was connected to the hydrogenation apparatus and evacuated. Hydrogen was then admitted under a pressure of 34 lbs./sq. inch above atmospheric, and the bottle shaken. After each fall of 16 lbs., corresponding to the absorption of 0·01 mol. hydrogen, the pressure was again increased to its original value.

At the beginning of the reduction the catalyst was chocolate brown in colour, but after a period of about two minutes it was reduced to platinum black.

The reduction was stopped after 0·039 mols. of hydrogen had been absorbed corresponding to a drop of 62·5 lbs. between the limits 34 and 18 on the Bourdon gauge. The catalyst was filtered off and the solvent evaporated, after which the residue was shaken up with freshly prepared sodium bisulphite solution in order to remove any unchanged aldehyde. On extraction with ether and removal of the ether, a pale yellow solid, m.p. 65°C, was obtained, which on recrystallisation from light petroleum ether (twice) melted at 80°C.

Yield 5 grams. (80%).

Colourless needles.

Preparation of Platinum Catalyst.

$$PtCl_4 + 4NaNO_3 \longrightarrow Pt(NO_3)_4 + 4NaCl$$

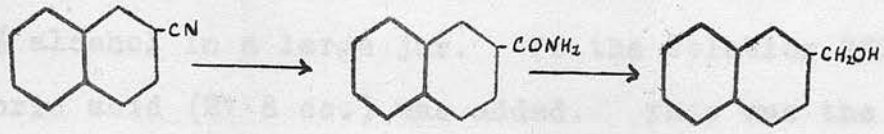
$$Pt(NO_3)_4 \longrightarrow PtO_2 + 4NO_2 + O_2$$

$$PtO_2 + H_2O \longrightarrow PtO_2.H_2O$$

(Cf. Adams, Voorhees, and Shriner, Org. Synth., 1928, 8, 92).

A.R. Sodium nitrate, (18 grams) was added to a solution of alkali-free platinum chloride (2 grams) in 6 cc. water in a small pyrex beaker, and the mixture was carefully evaporated to dryness. The temperature was gradually raised until fusion took place. Oxides of nitrogen were evolved and a brown powder separated. When the evolution of gas had moderated, the temperature was raised slightly, the mixture being stirred with a glass rod, and the melt was kept hot for ten minutes. The contents of the beaker were then cooled and treated with 50 cc. water. The brown oxide (1·2 grams) was washed by decantation, filtered through a hardened filter paper on a Gooch crucible, washed with water until free from nitrates, and dried in a vacuum desiccator.

Reduction of β-naphthoamide to β-naphthylcarbinol.



β-Naphthylcarbinol was also obtained from β-naphthoamide by reduction with sodium amalgam. This method was used by Byron West (J.A.C.S., 1920, 42, 1662), in the preparation of the corresponding α-compound.

(a) β-Naphthoamide.

Sodium hydroxide, (16 grams) was dissolved in 160 cc. 95% alcohol and filtered into a flask containing 60 grams pure β-naphthonitrile. The mixture was boiled under reflux for half an hour and cooled. The large crop of crystals of the amide which separated were filtered off and washed with alcohol. The filtrate was then boiled up as before for another half hour and a second crop of crystals obtained. The process was repeated a third time. After thorough washing with water to remove all sodium naphthoate, the amide was obtained as pure white needles.

M.p. 195°C.

Yield 40 grams. (64%).

(b) β-Naphthylcarbinol.

β-Naphthoamide (40 grams) was dissolved in 750 grams 95% alcohol in a large jar. To the solution 28% hydrochloric acid (27·8 cc.) was added. This was the theoretical amount required to form the hydrochloride of the amide. The apparatus was provided with a powerful mechanical stirrer reaching almost to the bottom of the jar.

4% Sodium amalgam (2,300 grams) was added gradually at the rate of 50 grams every fifteen minutes, each lot being accompanied by the addition of 10·25 cc. 28% hydrochloric acid. This was a molecular equivalent of the amount of amalgam and kept the acidity of the solution almost constant. After the final addition, the mixture was stirred for a further half hour. The solution was then made alkaline with caustic soda, filtered from sodium chloride and mercury, and the ethyl alcohol removed on a water bath. The β-naphthylcarbinol appeared as a brown oil which solidified on cooling.

On extraction with ether and removal of the ether, 32 grams of an oily solid were obtained. This was dissolved in light petroleum ether and on cooling the pure β-naphthylcarbinol was obtained.

Yield 10 grams (27%).

M.p. 80°C.

β-Naphthylmethyl chloride.

β-Naphthylcarbinol (12 grams) was dissolved in 50 cc. dry toluene and thionyl chloride (25 grams) was added in small quantities at a time. A vigorous reaction took place and the mixture was boiled under reflux till evolution of gases ceased, (about 3 hours). The toluene and thionyl chloride were then removed by distillation and the residue distilled in vacuo. On cooling, the distillate solidified to a white solid.

M.p. 47° - 48°C. B.p. 170°C/20 mm.

Quoted m.p. 48°C. B.p. 162°C/15 mm.

Yield 11 grams. (82%)

β-Naphthylmethyl magnesium chloride.

Magnesium turnings, (1·4 grams) were placed in a small flask and covered with 15 cc. dry ether. A solution of 10 grams β-naphthylmethyl chloride in ether was added together with a few drops of ethyl iodide. The mixture was kept boiling for a whole day but the Grignard compound could not be obtained.

β-Naphthylmethyl bromide.

β-Methylnaphthalene (28 grams) was placed in a

quartz flask fitted with a dropping funnel and a long air condenser. The flask was heated on a metal bath to a temperature of 240° - 260°C, and 32 grams bromine slowly dropped in. During the addition of the bromine the flask and contents were exposed to direct sunlight or to radiation from a mercury-vapour lamp. If the bromination was carried out without such radiation, the product was a glassy black solid from which no β-naphthylmethyl bromide could be obtained.

As soon as all the bromine had entered the flask, a current of air was passed rapidly through the mixture to drive out dissolved hydrobromic acid. The contents of the flask were then transferred to a Claisen flask and distilled in vacuo. A large amount of unchanged β-methylnaphthalene was invariably recovered, and the yield of β-naphthylmethyl bromide was extremely small, varying from 15% to 22% over a series of experiments.

The β-naphthylmethyl bromide solidified in the receiver and when crystallised from alcohol formed white plates.

M.p. 54°C. B.p. 213° - 215°C/100 mm.

β-Naphthylmethyl magnesium bromide and its reaction with acetyl chloride.

A solution of 9 grams β-naphthylmethyl bromide in

Grignard ether was added to a mixture of 1 gram magnesium turnings and 40 cc. dry ether in a 100 cc. flask fitted with a water condenser. Two drops of ethyl iodide were used to start the reaction. A vigorous reaction took place on heating, and when this had moderated, the flask was heated for fifteen minutes in order to complete the reaction.

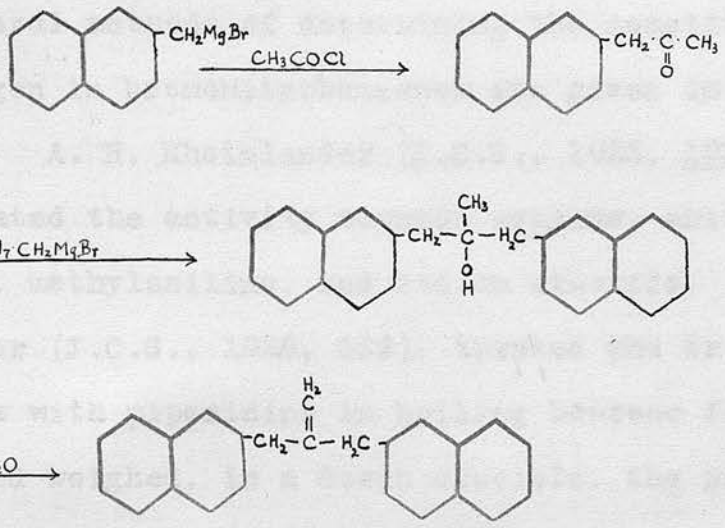
The mixture was thoroughly cooled in a mixture of carbon dioxide "snow" and ether, and filtered through glass wool into a similarly cooled solution of 5 grams acetyl chloride in ether. The white precipitate which immediately formed was decomposed with ice-cold dilute hydrochloric acid and the ether layer and ether extracts separated from the aqueous layer. On removal of the ether a white solid (4·5 grams) was obtained melting at 170° - 180°C. On recrystallisation from glacial acetic acid the melting point of the solid was raised to 184° - 185°C.

Analysis.

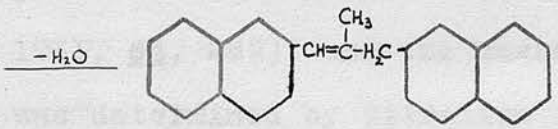
Found: C = 93·6%. H = 6·5%.

The analysis showed that the compound was a hydrocarbon so that it was probably obtained from the follow-

ing series of reactions:-



or 3:3'-dinaphthyl-isobutylene-1. (A).



1:3-dinaphthyl-2-methylpropylene. (B).

Required for A or B, $C_{24}H_{20}$.

C = 93·4%; H = 6·6%.

Semi-quantitative Experiments.

Several methods of determining the reactivity of the halogen in bromonitrobenzenes are given im the literature. A. H. Rheinlander (J.C.S., 1923, 123, 3099), investigated the activity towards aniline, aniline hydrochloride, methylaniline, and sodium ethoxide. Brewin and Turner (J.C.S., 1928, 332), treated the bromonitro compounds with piperidine in boiling benzene for several hours, and weighed, in a Gooch crucible, the precipitated piperidine hydrobromide.

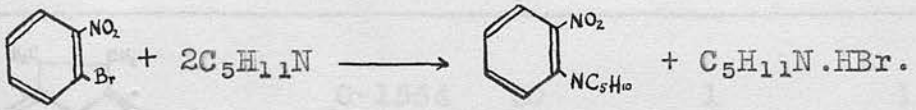
Piperidine has also been made use of by Salkind (Ber., 1931, 64, 289), and the amount of hydrobromide formed was determined by titration in aqueous solution with silver nitrate and potassium thiocyanate.

Salkind's method was used by us as it could be applied to smaller quantities of the bromonitro compounds.

Approximately 0·15 gram of bromonitro compound was weighed accurately in a test-tube provided with a ground glass stopper. 1 cc. of piperidine was added from a pipette and the tube immersed in a thermostat at 50°C. After a definite interval of time the contents of the tube were washed into a separating funnel with distilled water (about 50 ccs.) and shaken up with pure benzene. The benzene removed organic material from the aqueous layer while the halogen was left behind. In most cases a good

separation was obtained and the aqueous layer was left almost or completely colourless. The halogen in the solution was determined by Volhard's method, by titrating with silver nitrate and ammonium thiocyanate, ferric alum being used as indicator.

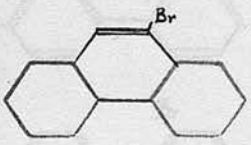
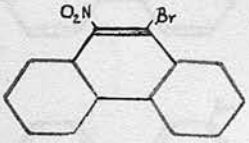
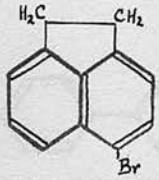
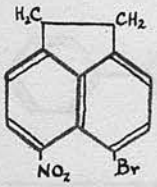
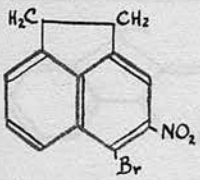
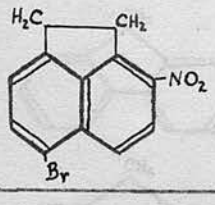
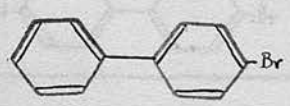
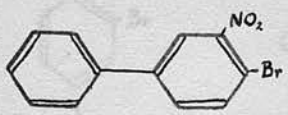
In reactive bromonitro compounds, the bromine was removed by piperidine giving piperidine hydrobromide and a compound of piperidine and the nitro-hydrocarbon e.g.

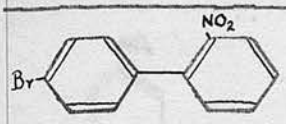
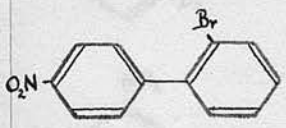
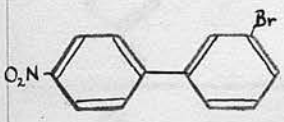
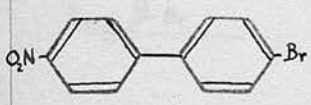
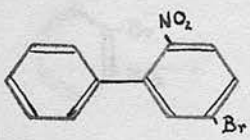
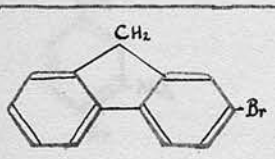
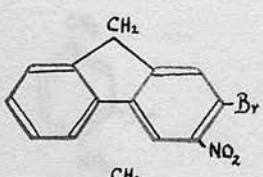
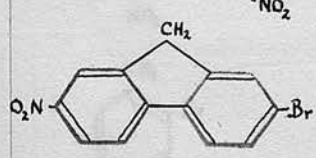
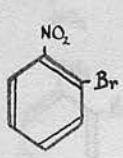


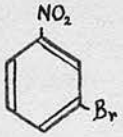
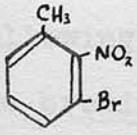
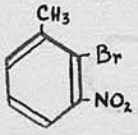
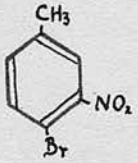
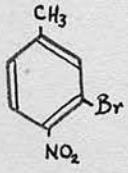
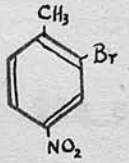
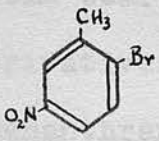
On mixing with water the piperidine hydrobromide went into solution with decomposition into piperidine and free acid, while the other organic material remained in suspension colouring the solution yellow. Before the amount of hydrobromic acid formed could be determined volumetrically the colour had to be removed, and extraction with pure benzene served.

For the titration, standard solutions of silver nitrate and ammonium thiocyanate of approximately N/50 concentration were prepared and standardised accurately.

RESULTS.

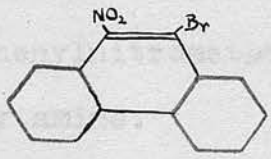
Compound	Weight (gms.)	Temp. (°C)	Vol. Piperidine (cc.)	Time (hrs.)	% Br_2 Removed
	0·1476	50	2	20	0
	0·1410	50	2	1	68·5
	0·1532	50	2	20	100
	0·1564	50	1	1	0
	0·1482	50	1	20	0
	0·1477	50	1	1	0
	0·1607	50	1	20	0
	0·1443	50	1	1	67·9
	0·1574	50	1	20	100
	0·1548	50	1	20	2·3
	0·1607	50	1	20	0
	0·1688	50	1	1	78·2
	0·1479	50	1	20	97·8

Compound	Weight (gms.)	Temp. (°C)	Vol. Piperidine (cc.)	Time (hrs.)	% Br_2 Removed
	0·1483	50	1	20	0
	0·1528	50	1	20	0
	0·1630	50	1	20	0
	0·1539	50	5	20	0
	0·0432	50	1	20	0
	0·1527	50	1	20	0
	0·1492	50	1	1	48·9
	0·1552	50	1	20	96·6
	0·1641	50	5	20	0
	0·1528	50	1	1	52·6
	0·1500	50	1	20	95·5

Compound	Weight (gms.)	Temp. (°C)	Vol. Piperidine (cc.)	Time (hrs.)	% Br_2 Removed
	0·1746	50	1	1	0
	0·1537	50	1	20	0·2
	0·1734	50	2	20	95·8
	0·1543	50	2	1	104
	0·1749	50	1	1	2·6
	0·1607	50	1	20	61·8
	0·1632	50	1	1	1
	0·1526	50	1	20	4·4
	0·1559	50	1	1	13·2
	0·1483	50	1	20	90·4
	0·1680	50	1	1	54·2
	0·1501	50	1	20	98·7
	0·1551	50	1	1	0
	0·1631	50	1	20	0
	0·1579	50	1	1	0·4
	0·1627	50	1	20	7·2

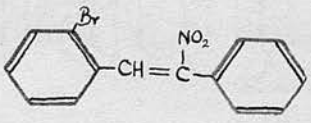
D I S C U S S I O N

In order to test the applicability of the method used for the detection of a double bond or conjugated system of double bonds, it was intended to prepare the following compounds and to examine the reactivity of the bromine in each.



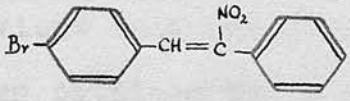
9-bromo-10-nitrophenanthrene

I



2-bromo-7'-nitrostilbene

II



4-bromo-7'-nitrostilbene

III

The conjugation of double bonds between the carbon atoms bearing the nitro and bromo groups in the stilbene derivatives is unquestionable, while the reactions of phenanthrene strongly indicate the presence of a double

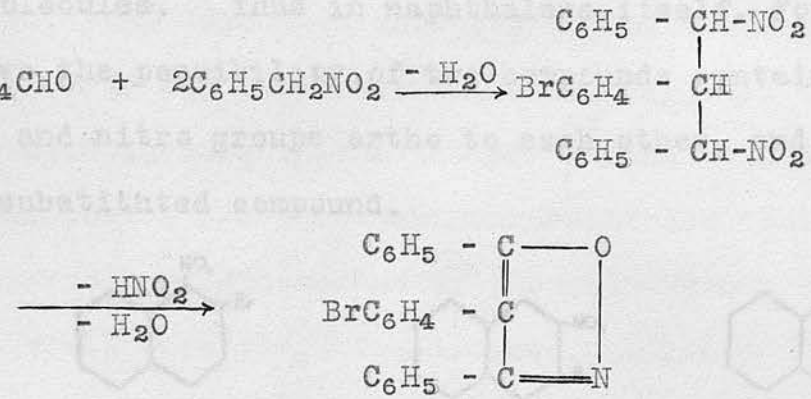
bond in the 9:10 position.

The 9-bromo-10-nitrophenanthrene was readily obtained, and subsequent reactivity measurements showed the bromine in this compound to be highly activated in contrast to the non-reactivity of the halogen in 9-bromophenanthrene, showing that in the former case, activation was entirely due to the presence of the nitro group through a -C=C- linkage.

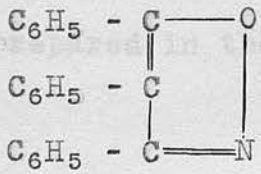
The attempts to prepare the bromonitrostilbene derivatives were, however, unsuccessful. The method used was that of Knoevenagel and Walter (Ber., 1904, 37, 4509), who obtained 7-nitrostilbene by condensing benzaldehyde with phenylnitromethane in the presence of an aliphatic primary amine.

Analysis of the compounds obtained in our case showed that the molecule contained 21 carbon atoms along with one atom each of nitrogen, oxygen, and bromine. It was therefore obvious that the desired stilbene derivatives had not been obtained and a search through the literature suggested that isoxazole derivatives had been synthesised.

The formation of the isoxazoles is brought about by the condensation of two molecules of phenylnitromethane with one molecule of aldehyde and the subsequent loss of nitrous acid and water according to the equation:-



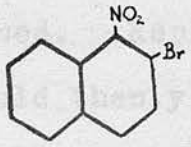
Heim (Ber., 1911, 44, 2021), who also studied this type of condensation, isolated besides other products triphenyisoxazole.

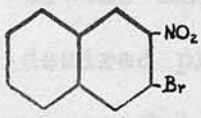


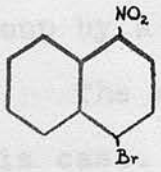
A part of this thesis deals, as stated in the Introduction, with the preparation of bromonitro derivatives of acenaphthene, diphenyl, and fluorene, and the subsequent examination of the reactivities of the halogen in these compounds towards piperidine. An attempt was therefore made to prepare as many derivatives as possible which would provide evidence as to the positions of the double bonds in these molecules.

In the cases of acenaphthene and fluorene, the number of such derivatives suitable for our purpose is reduced (due) to the presence of the methylene groups in

the molecules. Thus in naphthalene itself, for example, we have the possibility of two compounds containing bromo and nitro groups ortho to each other, and one such para-substituted compound.

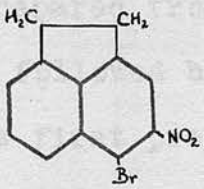


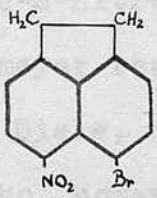




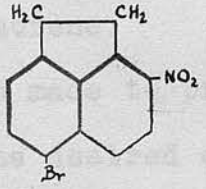
In acenaphthene, however, which may be considered as a 1:8 disubstituted naphthalene, there is no possibility of obtaining either a 1:2 or a 1:4 bromonitro derivative.

The compounds prepared in the acenaphthene series were:-





and a derivative whose structure is uncertain, but is probably that given below, for the reasons set forth in the Experimental Section.

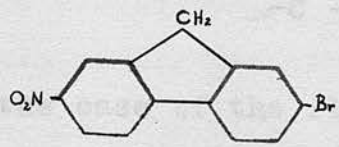


To complete the series a 2:3-bromonitroacenaphthene is necessary, but so far such a compound has resisted all attempts at preparation. By reference to Bell's work

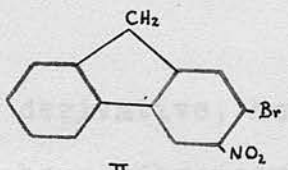
(J.C.S., 1932, 2732) on the powerful ortho-directing influence of the p-toluenesulphonamido group, (applied later with success in the toluene series), it was considered that a 3-bromo-2-aminoacenaphthene could possibly be obtained. Replacement of the amino group by a nitro group would then yield the desired product. The above method, however, proved unsuccessful in this case.

Only two bromonitro derivatives of fluorene have been prepared, one of which was already known.

They are:-



I



II

II was prepared from 2-amino-3-nitrofluorene by diazotisation followed by a Sandmeyer reaction. This nitroamine was first prepared by Diels, Schill and Tolson (Ber., 1902, 35, 3285), who, however, believed the compound to be 1-nitro-2-aminofluorene. This conclusion was later shown to be erroneous by Eckert and Langecke (J. prakt. Chem., 1928, 118, 263), who proved the compound to be 2-amino-3-nitrofluorene.

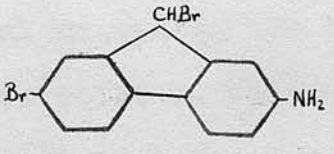
An attempt was also made to prepare a 1:2 disubstituted derivative, but the desired compound could not be obtained. For this purpose the 2-p-toluenesulphonamidofluorene was prepared and brominated in chloroform solution. By this procedure it was hoped that the 1:3-

dibromo-2-aminofluorene would be obtained.

McLeish and Campbell (J.C.S., 1937, 1103), using a similar procedure, obtained 1:3-dibromo-2-naphthylamine from β-naphthylamine, which on reduction with tin and hydrochloric acid gave 3-bromo-2-naphthylamine, the bromine in the 1-position being removed in the reduction. In this case, therefore, the bromine attached to a carbon atom linked to a carbon atom bearing an amino-group by a double bond, was easily removed.

$$\begin{matrix} -C & - & NH_2 \\ \| & & \\ -C & - & Br \end{matrix}$$

In the case of the fluorene derivative, however, which, on analysis, was shown to be a dibromoaminofluorene, repeated attempts to remove one of the bromine atoms by reduction resulted in the recovery of unchanged dibromoamine. In view of this fact, it seemed unlikely that one of the halogens occupied position 3 in the molecule, and it was thought possible that substitution had taken place in positions 7 and 9.



Position 7 in the fluorene molecule is known to be readily substituted and as 9-bromo-2-nitrofluorene is the chief product of the bromination of 2-nitrofluorene, position 9 was considered a likely point of attack for

the second halogen.

To test this theory, it was decided to eliminate the amino group by the standard methods, and to oxidise the remaining dibromofluorene to the fluorenone. Then if the bromine atoms occupied positions 7 and 9, the known 2-(7)-bromofluorenone should be formed.

In actual fact the ketone formed was shown to be an unknown dibromofluorenone. This fact at least showed that the dibromoaminofluorene obtained was not the 7:9-dibromo-2-aminofluorene.

Since the ketone finally obtained was not the already known 1:3-dibromofluorenone, (different melting points) (Montagne, Rev. Trav. Chim., 1909, 28, 449), the original dibromoaminofluorene could not have been the desired 1:3-dibromo-2-aminofluorene.

In view of the reactivity of the 3-position when position 2 is already occupied by a substituted amino group, a fact already demonstrated in the nitration of 2-acetamidofluorene, it seems probable that the dibromoamine obtained was the 3:7-dibromo-2-aminofluorene.

The non-removal of one of the bromine atoms by reduction, however, is still anomalous. Although this takes place in certain isolated cases (cf. naphthalene above) not enough work has been done on this subject to warrant (merit) any general ruling.

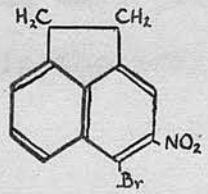
Most of the bromonitro diphenyl derivatives were

already known. The compounds were chosen in such a way that one substituent occupied the 4 position in one ring, while the other group, substituted in the other ring, was separated from the former by an increasing number of bonds. It was intended that a study of these compounds would show just how far along a conjugated system of double bonds the activation effect could be propagated.

A new bromonitrodiphenyl, namely the 4-bromo-3-nitro-derivative, has been prepared in the course of this work, from the known 4-amino-3-nitrodiphenyl.

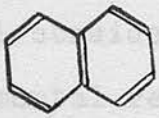
An attempt was made to convert the amino group in 2-amino-5-bromodiphenyl, to a nitro group, using the diazotisation method of Hantzsch and Blagden (Ber., 1900, 33, 2554). The yield, however, was extremely low, and, although the analysis figures for the compound were in good agreement with those required for a bromonitrodiphenyl, some doubt was entertained as to the identity of this compound on account of its very high melting-point, which was far beyond that of any isomer in the series.

Of the three compounds examined in the acenaphthene series only one contained reactive bromine, namely the 4-bromo-3-nitroacenaphthene.

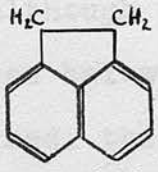


It would thus appear that the arrangement of bonds in acenaphthene is similar to that in naphthalene, since a double bond exists between carbon atoms 3 and 4. A final conclusion cannot be reached, however, until the halogen activity in a 2:3 bromonitro derivative is examined.

When we consider the fact that acenaphthene is merely a 1:8-disubstituted naphthalene derivative, the above conclusion is not unexpected.

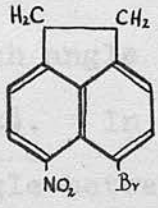


Naphthalene



Acenaphthene

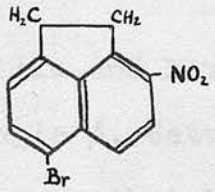
Particularly interesting and important was the non-reactivity of the bromine in the peri-substituted bromonitroacenaphthene; this was predicted from Fuson's theory.



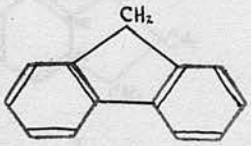
This non-reactivity seemed to indicate that the activation really was due to the presence of a double bond or conjugated system of double bonds in a fixed position, and not to the mere proximity of the groups. Further, substituents in the peri-positions are normally

very reactive, yet in the bromonitro series the bromine atom was not activated by the nitro group.

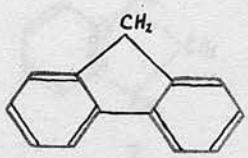
As was expected, the derivative whose structure is given as probably being as follows, gave no reactive bromine.



The structure of fluorene, as given in the literature, is generally as in I, although from the purely theoretical considerations given below, as well as from the experimental results obtained, the more likely form is represented by II.



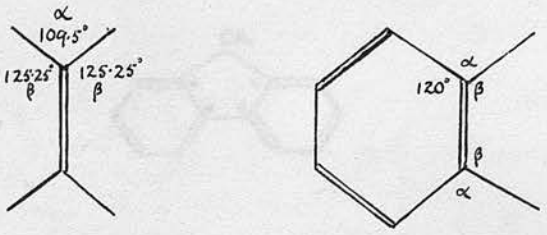
I



II

According to the tetrahedral theory of the structure of the carbon atom, each angle between two single bonds in methane is 109·5° (α). In a doubly bound carbon atom therefore, the angle between a single and a double bond will be $\frac{1}{2}(360 - 109{\cdot}5) = 125{\cdot}25°$, ($\beta$) (Mills and Nixon, J.C.S., 1930, 2510). When six carbon atoms unite forming an aromatic ring, the external angles α and β will be slightly greater than the above figures, since, as the ring is a regular planar hexagon, the internal

angles are reduced to 120°.



According to Mills and Nixon, however, the main point is that the angle β, between a double and single bond, is greater than α, that between two single bonds, the former approximating to 125° and the latter to 109°.

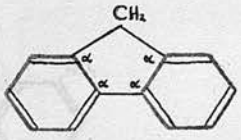
The above workers applied these considerations to the structure of hydrindene, and showed that theoretically the more stable form would be I and not II.

I II

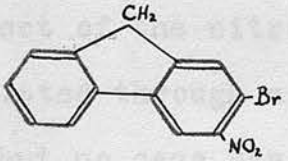
If the five-membered ring is regular, then each internal angle would be 108° which approximates very closely to an α angle. Form I would necessitate the inclusion of two α-angles in the five-membered ring whereas form II on account of the two β-angles shown would involve a greater strain in the molecule.

If we apply a similar argument to the fluorene molecule, it will be readily recognised that in order that the molecule should be as strain-free as possible, the five-membered ring should include four α-angles thus

giving the following as the more stable structure.

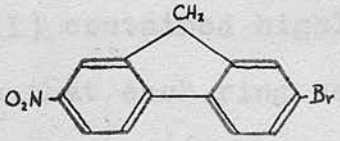


Of the two bromonitrofluorenes studied only one showed reactive bromine. This compound was the 2-bromo-3-nitrofluorene, and as the reactivity of the halogen indicates the existence of a double bond between carbon atoms 2 and 3, we have here experimental evidence in favour of the formula given above for fluorene.

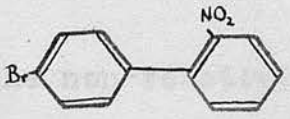


An examination of halogen reactivity in a 1:2-bromonitro derivative, is however, necessary to complete the evidence in favour of the above structure.

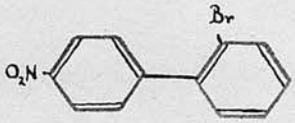
A surprising fact was the non-reactivity of the bromine in the 2-7 bromonitrofluorene, although in this compound the carbon atoms bearing the substituent groups are linked by a conjugated system of double bonds.



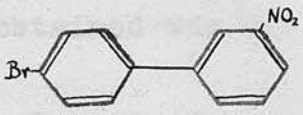
This anomaly is also shared by the bromonitro derivatives of diphenyl.



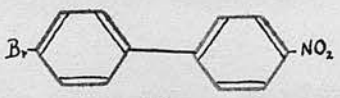
I



II



III

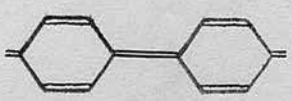


IV

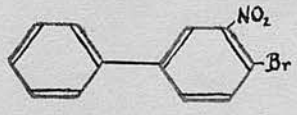
From Fuson's theory we would expect I, II and IV to contain reactive bromine, while the bromine in III should be non-reactive. Reactivity measurements on these compounds, however, showed that the halogen was inactive in all four cases.

It has been shown in the naphthalene series that the activating effect of the nitro group on the bromine atom can be transmitted through a conjugated system of two double bonds, but no case has been recorded of such activation through three or more double bonds. It may be therefore, that two such bonds is the limit for the transmission to take place, or that the effect is limited to one particular aromatic ring and cannot be propagated from one ring to another.

The quinonoid structure for diphenyl (I), must also be taken into account, but the fact that 4-bromo-3-nitrodiphenyl(II) contained highly reactive bromine seems to indicate that each ring retains its individual aromatic structure.



I



II

The non-reactivity of the bromine in the supposed 5-bromo-2-nitrodiphenyl probably indicates that the compound obtained was not the desired derivative.

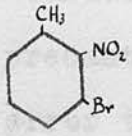
Note. Reactivity measurements were also carried out on monobromo derivatives of acenaphthene, fluorene and diphenyl but in all cases no evidence of halogen activity was observed.

Despite the claims of those who advocate a resonance "formula" for aromatic compounds, the cumulative evidence cited in this thesis appears to indicate that as far as the chemical properties of these compounds are concerned, the bonds in most cases are fixed in definite positions.

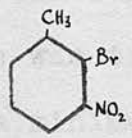
It would appear that each aromatic ring of a polynuclear compound tends to assume the bond structure which most nearly approaches the condition of an isolated benzene ring, and that the chemical properties of the compound are governed entirely by that structure.

In dealing with resonance it must be remembered that the theory has been evolved from purely physical data, and its relationship to chemical reactivity has not yet been investigated.

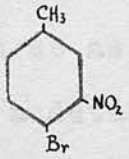
The second section of the work involved the preparation of the bromonitrobenzenes and several bromonitrotoluenes. A comparative examination of the reactivities of the halogen atoms in these compounds should reveal the effect of the presence of other groups (in this case the methyl group) in the activity of the halogen. In the toluene series the following compounds were prepared.



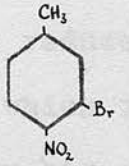
I



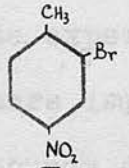
II



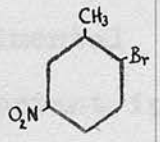
III



IV



V



VI

With the exceptions of I and IV these were prepared by standard methods, the procedure adopted by Gibson and Johnstone (J.C.S., 1929, 1243) being eminently satisfactory. Compound I was prepared from the p-toluenesulphonyl derivative of o-toluidine, which was brominated in pyridine solution (Bell, J.C.S., 1932, 2732), the resulting product on hydrolysis giving 3-bromo-2-aminotoluene. The amino group was then replaced by a nitro group by means of the diazotisation method of Hantzsch and Blagden (loc. cit.). The product was purified by steam distillation, and finally recrystallisation. Compound IV was obtained by brominating aceto-p-toluidide, the amino group of the subsequent hydrolysis

product being replaced by a nitro group as in the former case.

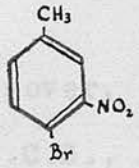
The method of estimating the reactivity of the halogen is detailed on p.89 of the Experimental Section. The results may be termed semi-quantitative since it was found that the figures were not absolutely reproducible, the margin of error being about 5%. The estimation of halogen reactivity was carried out under exactly the same conditions for each compound, and the same standard solutions were used in each titration. This precaution was taken so as to reduce the experimental error to a minimum, a detail which is more important in this case than with the polycyclic compounds dealt with in Section I. In the section under consideration the important factor was the variation in degree of activity and not, as formerly, the mere activity or non-activity of the halogen.

The reactivity of the bromine in 3-bromo-4-nitrotoluene (IV), lies very close to that given for o-bromonitrobenzene and is indeed probably identical with that of the latter, since the difference in the figures quoted lies within the limits of experimental error. In this compound therefore, the methyl group exerts no effect on the mobility of the halogen atom.

A curious anomaly appears to be present in the 3:4-disubstituted toluene in which the bromo and nitro groups

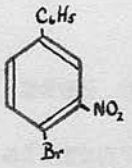
are reversed (III). The reactivity figure after 20 hours does not indeed lie far below that quoted for the 3-bromo-4-nitrotoluene although it is outside the limits of error. A comparison of the figures after one hour's reaction, however, shows a very definite decrease im the halogen activity.

It is also interesting to compare the reactivity of the halogen in 4-bromo-3-nitrotoluene with that in 4-bromo-3-nitrodiphenyl.



1 hour - 13·2% Br

20 hours - 90·4% Br

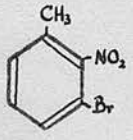


1 hour - 78·2% Br.

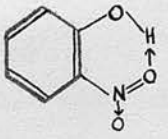
20 hours - 97·8% Br.

The results indicate that the phenyl group exerts much less effect than the methyl group.

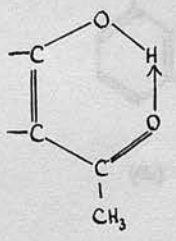
An examination of the 3-bromo-2-nitrotoluene (I) revealed that in this compound the reactivity of the bromine was reduced to a very large extent, only 2·6% bromine being removed in one hour, and 62% in 20 hours. There seems at first sight to be no reason why the halogen in this compound should be so unreactive but a possible explanation is that in this compound there is a tendency for the bonds to be fixed in such a manner that a single bond exists between carbon atoms 2 and 3.



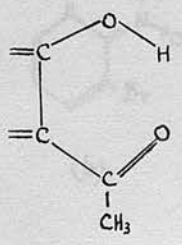
It is possible that we are dealing with a chelated compound, as in the case of o-nitrophenol or o-nitrotoluene (Sidgwick and Callow, J.C.S., 1924, 125, 527). It is well known that chelation occurs between the nitro and hydroxyl groups in o-nitrophenol, the hydrogen atom of the hydroxyl group being joined to an oxygen atom of the nitro group by a coordinate linkage.



Moreover, evidence has already been obtained by Baker (J.C.S., 1934, 1684), that preferential stabilisation of one Kekulé form of certain benzene derivatives does take place. From a study of various o-hydroxyacetophenones, this investigator came to the conclusion that the formation of a 6-membered chelate ring containing coordinately linked hydrogen, as shown in formula A, is dependent upon the presence of a double bond between the carbon atoms bearing the hydroxyl and acetyl groups. The conjugation of this double bond with that of the acetyl group apparently stabilises the coordinate linkage, and if no double bond is available at this position, as in B, chelation does not occur.

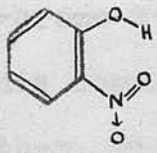


A

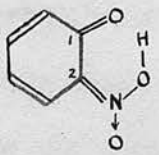


B

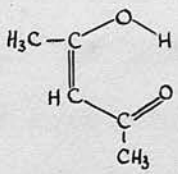
At this point it may be mentioned that the older idea of the coordinate linkage involving hydrogen has been replaced by the new theory of resonance (see Introduction). Quantum mechanics has shown that co-ordinately linked hydrogen is impossible, and on the basis of the theory, o-nitrophenol is represented as a resonance-hybrid of the following two structures, I and II analogous with those of acetylacetone in the aliphatic series III and IV.



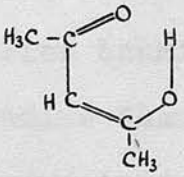
I



II



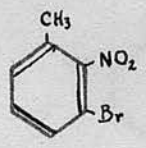
III



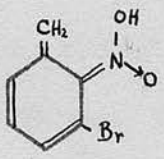
IV

This fact makes no difference to the point of the argument, however, namely that in a chelated compound such as o-nitrophenol, there is some tendency for the bonds to be fixed in such a manner that a single bond exists between the carbon atoms bearing the chelated groups. Thus in the quinonoid structure II above, we have a single bond joining carbon atoms 1 and 2.

On the basis of the above theory it would seem that the 3-bromo-2-nitrotoluene exists as a resonance hybrid of the following two forms:-



(a)

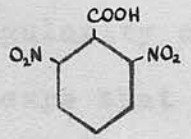


(b)

The comparative non-reactivity of the halogen in this compound is then evident, since, according to the theory of vinylogy outlined in the Introduction, a double bond is necessary between carbon atoms 2 and 3 for activation of the bromine by the nitro group to take place. That complete fixation of the bonds in the form of (b) does not take place is shown by the fact that a considerable percentage of bromine is removed in course of time.

An interesting derivative was encountered in the 2-bromo-3-nitrotoluene (II). Of the series examined this compound contained less reactive bromine than any other, with the exception of the 2-bromo-4-nitrotoluene (V), which, since the bromine atom is in the meta position with regard to the nitro group, yielded no bromine even after 20 hours.

A possible factor reducing the halogen activity in II was thought to be steric hindrance. The fact that the presence of two groups ortho to a substituent has a definite inhibitive effect on the chemical activity if that substituent has already been substantiated in many cases. For example, we may consider the reactivity of the carboxyl group in 2:6-dinitrobenzoic acid.



Esterification of this acid has been found to be very difficult and once it has been accomplished, hydrolysis of the ester requires much more vigorous treatment than usual. This fact has been attributed to the close spatial proximity of the nitro groups which act as a barrier inhibiting the normal reactivity of the carboxyl group.

A review of the literature, however, dealing with the subject of steric hindrance, shows that this phenomenon only occurs when the reacting group - COOH, CN, CO, CHO, etc - is unsaturated.

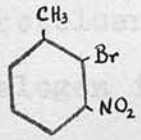
In 2-bromo-3-nitrotoluene however, the reactive group is a bromine atom, and it is extremely doubtful if steric hindrance can be held responsible for the diminution of its reactivity.

Another striking diminution in the reactivity of the bromine atom was observed in the case of 2-bromo-5-nitrotoluene (VI). In view of the somewhat high halogen activity encountered in the analogous p-bromonitrobenzene it is somewhat surprising to find such a low figure in the case of the former compound.

Our results indicate that the presence of other groups in the molecule tend to reduce the activation effect conferred on a bromine atom by a nitro group.

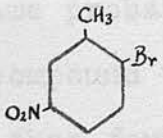
A striking regularity occurs throughout the series examined. It appears that the halogen activation is

modified if the methyl group occupies the meta position to the nitro group or the ortho position to the bromine atom. The effect is also apparent to a smaller extent if the methyl group is substituted in the para position with respect to the halogen. This is illustrated in the following compounds whose reactivities are also quoted, the figures being the percentage bromine liberated after one hour, and after 20 hours.



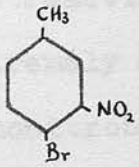
1·0

4·4



0·4

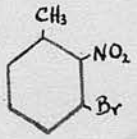
7·2



13·2

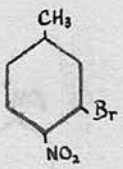
90·4

Disregarding the 2-bromo-4-nitrotoluene (V) for reasons already stated, we have still two compounds in which the above conditions for deactivation do not apply and which therefore, should show highly reactive halogen. These are 3-bromo-2-nitrotoluene and 3-bromo-4-nitrotoluene which are shown below with their respective figures.



2·6

61·8

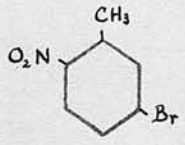


54·2

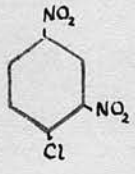
98·7

The low reactivity measurements obtained for the former compound have already been accounted for by the theory of chelation previously outlined. The latter compound, moreover, is in complete agreement with the rule given above since the reactivity measurements approximate very closely to those obtained for o-bromonitrobenzene.

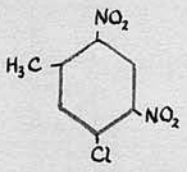
Applying the theory outlined to the unknown 3-bromo-6-nitrotoluene it seems probable that the reactivity of the halogen in this compound would be extremely high, probably approaching that found in p-bromonitrobenzene.



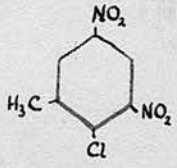
The work of Lindemann and Pabst (Ann., 1928, 462, 24) although concerned with more complicated molecules than those dealt with here is in accordance with the theory outlined above. The following compounds were studied by these workers and the figures give the reactivity measurements of the halogen in each after reacting with aniline for 10 minutes.



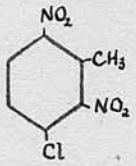
83%



40%



12%



0%

The non-reactivity of the last compound does not fit in with our theory, but may be due to complications arising from chelation of the methyl-groups with two nitro groups.

The final part of the work deals with an attempt to study the problem of the structure of naphthalene by a method based on the results obtained by Gilman and coworkers (p. 14) in their study of the reactions of α-naphthylmethyl magnesium chloride with various reagents.

The chief difficulty encountered was the preparation of β-naphthylmethyl halide. Gilman, working with the corresponding α-compounds, found that the α-naphthylmethyl chloride prepared by direct chlorination of α-methylnaphthalene, reacted only with difficulty to give a Grignard reagent but that the same compound prepared via the alcohol readily formed the desired Grignard compound. It was therefore decided in our case to apply the second method.

The β-naphthylcarbinol was prepared by two methods, (a) reduction of β-naphthaldehyde; and (b) reduction of β-naphthoamide.

(a) The aldehyde was obtained in 50% yield by a new method involving the reduction of β-naphthoyl chloride with gaseous hydrogen, using palladium-barium sulphate as catalyst. The process, however, was wasteful, although the yield of aldehyde exceeds that of any other method quoted in the literature.

The aldehyde was reduced to β-naphthylcarbinol by

hydrogenation under pressure in the presence of platinum black. The method has the advantage of giving a pure product which can be easily and directly isolated.

(b) The β-naphthylcarbinol was obtained by a method similar to that used by West (J.A.C.S., 1920, 42, 1662) in the preparation of α-naphthylcarbinol.

β-Naphthoamide was reduced to the alcohol by treatment with sodium amalgam and hydrochloric acid. This was undoubtedly the better method although the yield did not exceed 30%.

The preparation of β-naphthylmethyl chloride from the alcohol was accomplished without difficulty, but in view of Gilman's finding with regard to the α-naphthylmethyl chloride it was rather surprising to find that our compound would not form a Grignard reagent, even after prolonged heating, addition of methyl magnesium iodide etc.

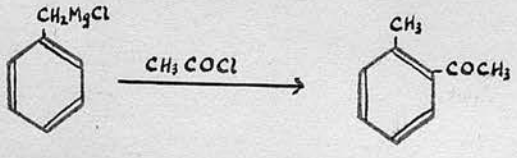
An attempt was also made to prepare the β-naphthylcarbinol for the above work using the method of Ziegler (Ber., 1921, 54, 737) which proved successful in Gilman's case. This consisted of treating the Grignard reagent formed from β-naphthyl iodide or bromide with gaseous formaldehyde, generated by heating trioxymethylene or paraformaldehyde. The method, however, proved unsuccessful, the chief product being β:β'-dinaphthyl.

A general method for the preparation of aldehydes,

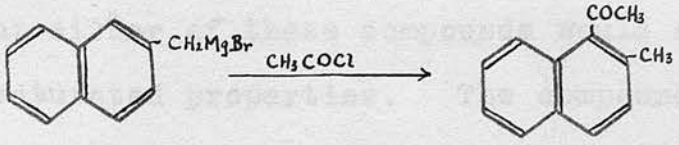
given by Stephen (J.C.S., 1925, 127, 1874) was used in an attempt to prepare β-naphthaldehyde from β-naphthonitrile but only traces of the desired product were obtained.

In view of the failure to obtain a Grignard reagent with the β-naphthylmethyl chloride prepared as above, it was decided to prepare β-naphthylmethyl bromide by direct bromination of β-methylnaphthalene and to attempt to prepare the required Grignard compound from this. Bromination of β-methylnaphthalene at high temperatures under ordinary conditions, led to the production of compounds which probably contained halogen substituted in the ring, and no β-naphthylmethyl bromide could be isolated from the resulting mixture. Bromination in a quartz flask in direct sunlight or under radiation from a mercury vapour lamp, however, yielded the required halide, although the yield was unsatisfactory, the maximum being only 22%. The β-naphthylmethyl bromide prepared by this method readily yielded the desired Grignard reagent.

Before examining the reaction of this reagent with acetyl chloride it was decided to repeat Gilman's work on the reaction between benzyl magnesium chloride and acetyl chloride. In the latter case the findings of the above worker were substantiated in that a large percentage of the product consisted of 2-methylacetophenone, formed according to the equation

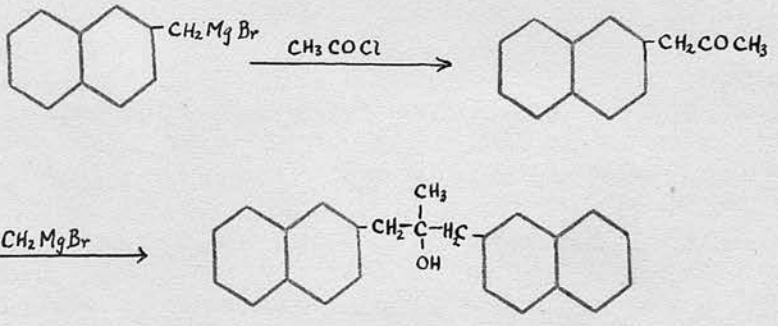


A similar reaction was therefore performed on the β-naphthylmethyl magnesium bromide in the expectation of obtaining methyl-β-methyl-α-naphthyl ketone (I).



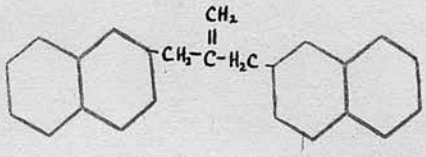
I

The compound obtained, however, on analysis was found to be a hydrocarbon, which in all probability was formed by the abstraction of the elements of water from the normal product of the reaction (II) as follows:-

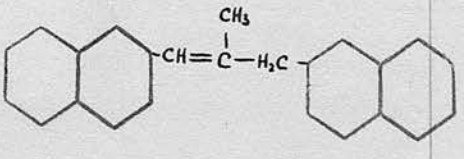


III

There are obviously two possible ways of splitting off water from II resulting in the formation of either 3:3'-dinaphthyl-isobutylene-1 (III) or 1:3-dinaphthyl-2-methyl-propylene (IV).



III



IV

The analysis figures obtained for the compound formed are in very good agreement with those required for III or IV.

It would be expected from the constitutions of III and IV that either of these compounds would exhibit highly unsaturated properties. The compound obtained, however, did not decolourise permanganate solution and only reacted very slowly with bromine water. These observations throw doubt on the formulae advanced especially when it is realised that similar compounds such as α:α-diphenylethylene - $\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!C=CH_2$ rapidly add on bromine and decolorise potassium permanganate.

S U M M A R Y.

Various bromonitro derivatives of acenaphthene, fluorene, and diphenyl have been prepared and the reactivities of the bromine atoms towards piperidine measured.

With the exception of those diphenyl derivatives in which the bromo and nitro groups occupied positions in different rings, the results are in accordance with Fuson's vinylogy theory.

In some instances the results have been used to shed light on the arrangement of double bonds in aromatic compounds.

A comparison has also been made of the reactivities of the bromine atoms in the bromonitrobenzenes with those of the bromonitrotoluenes, the results indicating that the presence of another substituent in the ring modifies the halogen activity to a various extent depending on the position of the substituent.

An unsuccessful attempt to study the problem of the structure of naphthalene by another method has also been described.

In conclusion the author desires to thank Dr. N. Campbell for his helpful criticism and unfailing encouragement throughout the course of this research.